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The Crystal Structure of Silver Oxalate*

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(Received April 10, 1943)

An x-ray diffraction study reveals that silver oxalate is monoclinic, having the symmetry of the space group $P2_1/c-C_{2h}^5$. The unit cell has the following dimensions: $a=3.46\pm0.02$A, $b=6.16\pm0.02$A, $c=9.47\pm0.04$A, $\beta=76°\pm1°$. There are two molecules of $Ag_2C_2O_4$ per unit cell. All atoms are located in sets of fourfold general positions. The parameters of the silver and oxygen atoms are determined from two-dimensional Fourier syntheses, using the experimental crystal structure factors for the $h0l$ and $0kl$ planes. The positions of the carbon atoms are approximately determined by requiring that the carbon-carbon and carbon-oxygen bond distances be reasonable. The silver oxalate structure may be considered to be made up of chain molecules of composition $(Ag_2C_2O_4)_x$ extending through the lattice parallel to the b axis. These chains appear to be held together by longer silver-oxygen bonds to form the three-dimensional structure.

A knowledge of the crystal structure of silver oxalate is pertinent in attempting to deduce its mechanism of thermal and photo decomposition. Although the crystal structures of oxalic acid and a number of its salts have been investigated,[1–5] no previous analysis of the structure of silver oxalate has been published. The chief objective in the present investigation was to determine the location of the silver atoms and approximate position of the carbon and oxygen atoms in the silver oxalate structure. No attempt was made to attain great accuracy in measuring the intensities of the x-ray reflections.

Single crystals of silver oxalate were prepared by slow evaporation of a concentrated ammoniacal solution as described by Macdonald.[6] The resultant crystals, the largest of which were about 3 mm in maximum dimension, were in the shape of relatively thick plates, appearing to have a twofold axis normal to the plane of the plate. Many of the crystal faces were rough and poorly developed. Macdonald[6] stated that single crystals of silver oxalate prepared by him had been examined by F. Walker who concluded that they were either monoclinic or triclinic with an extinction angle ($Z\wedge c$) of 16 degrees and a refractive index considerably greater than 1.72. Also, the crystals were found to have two well-defined cleavages at 83 degrees to one another.

Rotation and zero, first, and second-layer equi-inclination Weissenberg photographs were obtained, using Cu $K\alpha$ radiation, for rotation about the axis normal to the plane, and for rotation about a principal axis lying in the plane, of a platelike crystal. These photographs showed

* Communication No. 923 from the Kodak Research Laboratories.

[1] W. H. Zachariasen, Zeits. f. Krist. **89**, 442 (1934).

[2] S. B. Hendricks, Zeits. f. Krist. **91**, 48 (1935).

[3] S. B. Hendricks and M. E. Jefferson, J. Chem. Phys. **4**, 102 (1936).

[4] J. M. Robertson and I. Woodward, J. Chem. Soc. 1817 (1936).

[5] R. Brill, C. Hermann, and C. L. Peters, Naturwiss. **27**, 677 (1939).

[6] J. Y. Macdonald, J. Chem. Soc. 832 (1936).

TABLE I. *h0l* crystal structure factors of silver oxalate.

		Theoretical Structure Factor		
h0l	$\|F\|_{exp}$	F_{Ag}	F_{Ox}	F
100	104	96	39	135
200	16	− 28	−10	− 38
300	72	− 88	−22	−110
400	36	− 77	−10	− 87
102	96	−135	56	− 79
$\bar{1}02$	56	74	−19	55
202	84	− 86	24	− 62
$\bar{2}02$	88	115	−25	90
302	6	− 2	− 2	− 4
$\bar{3}02$	56	72	− 5	67
104	24	14	5	19
$\bar{1}04$	96	−131	−22	−153
204	80	86	22	108
$\bar{2}04$	64	− 54	9	− 45
304	48	86	14	100
$\bar{3}04$	40	36	18	54
106	56	87	−18	69
$\bar{1}06$	44	28	20	48
206	8	14	− 3	11
$\bar{2}06$	52	− 61	30	− 31
108	64	− 72	− 3	− 75
$\bar{1}08$	80	80	31	111
208	40	− 86	−15	−101
$\bar{2}08$	72	93	15	108

that silver oxalate is monoclinic, its b axis being normal to the plane of the plate. The other axis of rotation of the crystal was identified with the a axis. The crystal used in obtaining the b axis photographs was ground to a disk shape about 1 mm in diameter and 0.5 mm thick with crystallographic b as its axis. The crystal used for a axis photographs was ground to a rod shape about 2 mm long and 0.4 mm in diameter with crystallographic a as its axis.

The symmetry of the Weissenberg photographs and the absence of *h0l* reflections for l odd and of 0*k*0 reflections for k odd established that silver oxalate has the symmetry of the space group $P2_1/c-C_{2h}^5$. The unit cell dimensions obtained from the zero-layer Weissenberg photographs are: $a=3.46\pm0.02$A, $b=6.16\pm0.02$A, $c=9.47\pm0.04$A, $\beta=76°\pm1°$. The density of silver oxalate is 5.029,[7] which requires that there be two (calculated, 1.99) molecules of $Ag_2C_2O_4$ per unit cell.

The experimental crystal structure factors were calculated from the observed x-ray intensities, whose relative values were obtained by visual comparison with a sensitometrically exposed strip, by making corrections for the Lorentz, the polarization, and the absorption factors. The corrections for absorption were

TABLE II. 0*kl* crystal structure factors of silver oxalate.

		Theoretical Structure Factor		
0*kl*	$\|F\|_{exp}$	F_{Ag}	F_{Ox}	F
002	66	−64	33	− 31
004	128	−97	−23	−120
006	112	99	−14	85
008	25	1	19	20
00,10	51	−86	18	− 68
011	120	−94	28	− 66
012	—	− 4	3	− 1
013	120	141	7	148
014	—	3	1	4
015	51	−21	− 1	− 22
016	—	1	− 1	0
017	66	−84	5	− 79
018	—	− 3	3	0
019	77	79	7	86
020	141	152	−37	115
021	—	8	− 3	5
022	96	−53	− 7	− 60
023	8	2	− 3	− 1
024	85	−88	24	− 64
025	8	− 7	1	− 6
026	112	96	13	109
027	11	3	7	10
028	21	1	− 6	− 5
029	5	4	5	9
02,10	61	−82	−11	− 93
031	122	−71	−31	−102
032	21	−11	− 7	− 18
033	120	113	5	118
034	8	8	0	8
035	11	−19	14	− 5
036	8	4	8	12
037	72	−80	0	− 80
038	5	− 9	4	− 5
039	51	76	−13	63
040	114	111	3	114
041	13	12	2	14
042	80	−41	− 5	− 46
043	8	2	4	6
044	77	−73	−15	− 88
045	11	−12	3	− 9
046	69	88	− 6	82
047	5	6	− 1	5
048	5	1	1	2
051	64	−55	9	− 46
052	7	−14	9	− 5
053	88	93	−15	78
054	11	10	4	14
055	45	−18	−17	− 35
056	—	6	− 6	0
057	48	−76	− 5	− 81
058	8	−14	− 7	− 21
060	90	94	2	96
061	16	15	1	16
062	37	−36	0	− 36
063	5	4	0	4
064	53	−64	− 4	− 68
065	11	−17	− 3	− 20
066	56	80	− 5	75
071	43	−48	− 7	− 55
072	21	−18	− 8	− 26
073	53	84	6	90

[7] *International Critical Tables* (McGraw-Hill Book Co., New York, 1926), Vol. 1, p. 124.

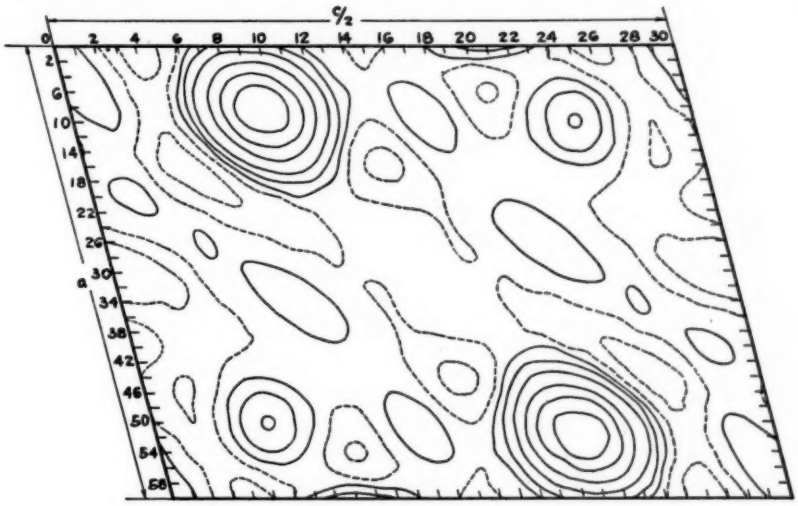

FIG. 1.

taken from the *Internationale Tabellen*,[8] using values of $\mu R=15$ and $\mu R=40$, respectively, for the $0kl$ and $h0l$ intensities. Because of the shape of the crystal used in obtaining $h0l$ intensities, the absorption correction is, in this case, probably not very accurate.

The special positions of the space group $P2_1/c$ are:[9]

(a) 000; $0\ \frac{1}{2}\ \frac{1}{2}$ (b) $\frac{1}{2}\ 00$; $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
(c) $00\ \frac{1}{2}$; $0\ \frac{1}{2}\ 0$ (d) $\frac{1}{2}\ 0\ \frac{1}{2}$; $\frac{1}{2}\ \frac{1}{2}\ 0$.

The fourfold general positions are:

(e) xyz; $\bar{x}\bar{y}\bar{z}$; $\bar{x}, 1/2+y, 1/2-z$; $x, 1/2-y, 1/2+z$.

A brief examination of the $h00$, $0k0$, and $00l$ x-ray intensities showed that the silver atoms could not occupy any of the centers of symmetry, (a), (b), (c), and (d), of the structure. They must then be in one set of fourfold general positions, (e). Preliminary values of the parameters for the silver atoms were obtained from a consideration of all $0kl$ and $h0l$ intensities, neglecting the contributions of the lighter atoms. The best agreement between experimental and theoretically calculated structure factors seemed to be obtained by assigning the following values to the parameters of the silver atoms:

$$x=0.145, \qquad y=0.495, \qquad z=0.156.$$

Tables I and II contain the experimentally determined relative crystal structure factors, F_{exp}, which have been adjusted to approximately the same scale as the theoretically calculated structure factors, F, and also the contributions, F_{Ag}, of the silver atoms and, F_{Ox}, of the oxalate groups to the theoretical structure factors. The contributions, F_{Ox}, are based on a structure which is to be described. The atomic scattering factors used in calculating theoretical crystal structure factors are found in the *Internationale Tabellen*.[10] As can be seen from Tables I and II there is fair general agreement between F_{Ag} and the experimental structure factors F_{exp}. This indicates that the silver atoms have been located in about the correct positions.

Since silver has a high atomic number compared to carbon and oxygen, the algebraic signs of most of the crystal structure factors are determined by the silver atoms. Therefore it is possible to make Fourier syntheses of the projections of the electron density of the unit cell parallel to the b axis and parallel to the a axis onto planes perpendicular to these axes, using the experimentally determined structure factors $F(h0l)$ and $F(0kl)$, respectively, and the algebraic signs as determined by the silver atoms. Such contour maps were prepared by summing the following two-dimensional Fourier series:

$$\left.\begin{aligned} A_{xz}\rho_{xz}&=\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} F(h0l)\cos 2\pi(hx+lz)\\ A_{yz}\rho_{yz}&=\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} F(0kl)\cos 2\pi(ky+lz)\end{aligned}\right\}. \quad (11)$$

[8] *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (Gebrüder Borntraeger, Berlin, 1935), Vol. 2, p. 585.

[9] Reference 8, Vol. 1, p. 101.

[10] Reference 8, Vol. 2, pp. 571 and 572.

In these equations the quantities A and ρ are, respectively, the areas of projections of the unit cell and the electron densities at points xz or yz on the projections. The values of F ($h0l$) and F ($0kl$) used are those listed under F_{exp} in Tables I and II. The algebraic sign of these factors was taken as that of the contribution F_{Ag} of the silver atoms in all cases where the silver atoms clearly determined the algebraic sign. Terms for small values of the structure factors were added in to form a second approximation, using the algebraic signs as determined by the positions of the atoms indicated in the first summation. The calculations were carried out by the method of Lipson and Beevers[11] at intervals of 1/60 along the z axis and 1/30 along the x and y axes.

Figures 1 and 2 show the projections parallel to the b and parallel to the a axes, respectively. Since the experimental crystal structure factors have only relative values, the exact value to be assigned to the term F (000) in the two summations was not known and the term was consequently omitted. This is equivalent to subtracting a constant density from all points on the projection. If the structure factors were on an absolute basis, F (000) would equal 276. Its correct value for these summations cannot be far from this figure since, as explained, the experimental structure factors were adjusted to approximately an absolute scale. Figures 1 and 2 are, therefore, contour maps of the relative electron density times the area of the projection minus a constant. Contour lines are drawn at intervals of 400 in these figures, except at the silver atoms, which are, of course, the highest peaks on the projections, where contours above 400 are included at intervals of 1000. All contours for negative values are shown as dotted lines. The highest contour shown on the silver atoms of the xz projection is 4000; that on the yz projection is 6000. This large difference is to be expected since the quantity plotted is the relative electron density multiplied by the area of the projection. There are several maxima on both the xz and yz projections which rise to a height of zero or a little greater. *Most* of these are probably false maxima which may be attributed to inaccurate values of the crystal structure factors and to discontinuing an infinite series after a finite number of terms. The latter cause is probably the most important, especially for a structure having atoms of relatively high atomic number, such as silver. This situation could be bettered if data obtained with shorter wave-length radiation, such as Mo $K\alpha$, were available or if a convergence factor were applied to the crystal structure factors used in making the summations.

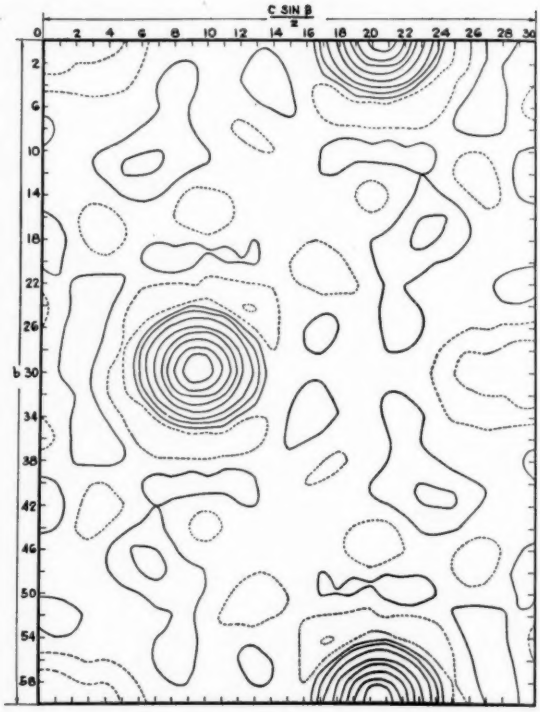

FIG. 2.

Attempting to locate oxygen and carbon atoms in the presence of silver atoms, with data no more extensive nor accurate than reported here, by the method of Fourier analysis, is perhaps overburdening the method. Certainly the expected accuracy of the results cannot be very great.

The parameters of the silver atoms can be determined quite accurately from Figs. 1 and 2 and are the same as the preliminary values. The next highest maxima on the projections should be the oxygen atoms. On the yz projection, Fig. 2, there are peaks which rise to a height of a little over 400 at the points $y=11.2/60$, $z=6.0/60$;

[11] H. Lipson and C. A. Beevers, Proc. Phys. Soc. **48**, 772 (1936).

at $y=47.1/60$, $z=6.6/60$ and at the equivalent points $y+1/2, z-1/2$. Although the zero contour for these maxima has a peculiar shape, the fact that no other maxima except those of the silver atoms are of equal or greater height makes it seem probable that these are the oxygen atoms. Corresponding maxima should appear at the same z value on the xz projection, Fig. 1. Here there is only one such maximum, that at $x=50.2/60$, $z=5.8/60$ which is repeated at the equivalent point $\bar{x}$, $z-1/2$. Since these maxima rise to a height of 800, it seems probable that they represent two oxygen atoms superimposed. If the maxima on the yz projection represent one oxygen atom and those on the xz projection represent two oxygen atoms superimposed, then the ratio of their heights should be $A_{yz}/2A_{xz}=56.5/(2\times31.8)=0.89$. If F (000) is assumed to be 300, then the observed ratio of the heights is $(400+300)/(800+300)=0.64$. The y and z parameters for the two crystallographically non-equivalent oxygen atoms, O^1 and O^2, were taken from the yz projection. The x parameter taken from the xz projection is rather uncertain because of the superposition of the oxygen atoms. The fact that the z parameter for the oxygen peak on the xz projections is not the mean of the z values of the two corresponding peaks on the yz projection is probably to be attributed to inaccuracies in the data and to the breaking off of the infinite Fourier series.

The location of the carbon atoms requires the selection of the correct maxima from the group which is left after the location of the silver and oxygen atoms. Since there are several maxima left having about the same height, and they cannot all be carbon atoms, some additional criteria must be used in selecting the position of the carbon atoms. The selection can be made if it is required that the carbon atoms be located so as to provide reasonable carbon-carbon and carbon-oxygen bond distances. There is only one set of maxima on the xz and yz projections which will meet these requirements. On Fig. 1 the finger-like maximum extending from the origin has a ridge along its center of height 220. A carbon atom might be located at any point along this ridge with a second carbon atom located by the operation of the center of symmetry at the origin. Thus there would be an overlapping of the carbon atoms on this projection producing an elongated maximum. On Fig. 2, the yz projection, the only maxima which can be selected to meet the requirement of reasonable bond distances are at $y=52.4/60$, $z=1/60$ and the crystallographically equivalent positions. Even here reasonable bond distances cannot be obtained by locating the carbon at the peak of the maximum but it must be displaced toward the origin to a value of $y=53.1/60$, $z=0.7/60$. It may be that the diffraction effects arising from the incomplete nature of the Fourier series have caused the maxima to be shifted away from the origin. The fact that the values on this projection fall off rapidly to large negative values at the origin makes this explanation seem more probable. This effect cannot be real since inclusion of a reasonable value of the F (000) term in the series will not make all these values positive. The parameters finally chosen for the carbon atom place it on the ridge of the maximum on the xz projection but displace it slightly toward the origin from the peak of the maximum on the yz projection.

The following are the parameters selected for the atoms in the silver oxalate structure:

	x	y	z
Ag	0.145	0.495	0.156
C	−0.070	0.115	−0.012
O^1	0.163	0.216	−0.110
O^2	−0.163	0.187	0.100

The error in the location of the silver atoms is probably small, about ±0.02A. In the case of the carbon and oxygen atoms, particularly the carbon atoms, the uncertainty is much greater. The contributions of the oxalate groups to the crystal structure factors, F_{Ox}, which are shown in Tables I and II, are calculated by using the above parameters. There is fairly good agreement between theoretical and experimental crystal structure factors. In calculating the experimental crystal structure factors no correction was made for thermal vibration of the atoms. Such a correction might improve the agreement between theoretical and experimental crystal structure factors.

Figures 3 and 4 show idealized drawings of the projections of the silver oxalate structure, as determined by the above parameters, the atoms

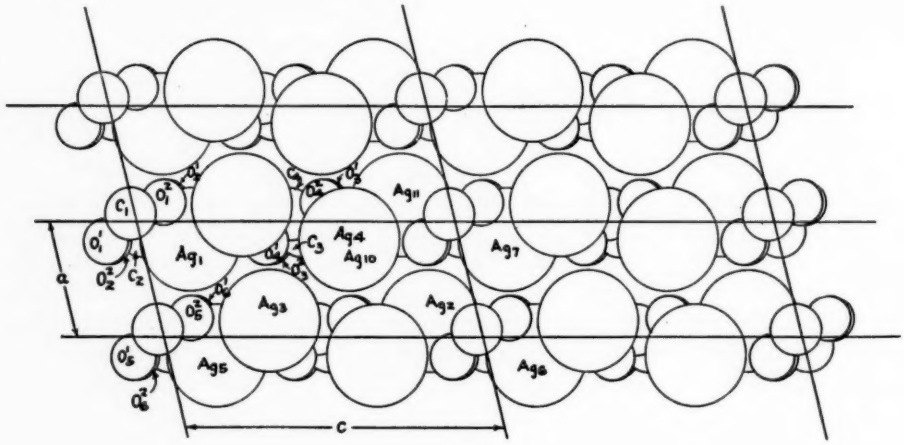

FIG. 3.

being represented by circles whose radii are proportional to the covalent radii determined by Pauling and Huggins.[12] The important interatomic distances are as follows (see Figs. 3 and 4):

$C_3-C_4=1.53$A	$O_4^1-O_1^2=3.27$A
$C_1-O_1^1=1.24$A	$O_1^1-O_6^2=3.42$A
$C_1-O_1^2=1.15$A	$O_1^1-O_1^2=2.04$A
$Ag_1-O_2^1=2.17$A	$Ag_2-Ag_6=3.34$A
$Ag_1-O_1^2=2.30$A	$Ag_2-Ag_7=3.35$A
$Ag_1-O_6^1=2.93$A	$Ag_5-Ag_3=3.58$A
$Ag_1-O_5^2=3.00$A	
$Ag_1-O_4^1=2.58$A	
$Ag_1-O_3^2=2.61$A	

The carbon-carbon and carbon-oxygen distances are, of course, somewhat arbitrary but the fact that they are reasonable distances as compared with corresponding distances in the known structures of other oxalates[1-5] indicates that the placement of the carbon atoms is approximately correct. The silver-oxygen distances should be slightly larger than the sum of the normal covalent radius of oxygen and the tetrahedral radius of silver, the increase being that accompanying a change of the coordination number of silver from four to six. On the basis of the work of Pauling and Huggins[12] the silver radius can be expected to increase by about six percent. This would make the sum of the silver and oxygen radii equal to 2.28A. This value is slightly larger than the $Ag_1-O_2^1$ distance of 2.17A but this is compensated by the other Ag−O distances being larger. The $Ag_1-O_6^1$ and $Ag_1-O_5^2$ distances are quite large compared to 2.28A, but since no atoms are situated between these, they may be considered as being coordinated. Each silver atom has a coordination number of six, and each oxygen atom a coordination number of three. The smallest oxygen-oxygen distances between oxygen atoms not bound to the same carbon atom are well above the minimum allowable distance, about 2.6A, for such compounds.

As can be seen from Figs. 3 and 4, the oxalate group is non-planar. The carbon atoms of a given oxalate group are displaced to opposite sides of the plane determined by the oxygen atoms of that group. By decreasing the x and z parameters of carbon to almost zero, the group can be made planar. In such a structure, however, the carbon-carbon and carbon-oxygen bonds are too short. If the C_1-C_2 distance is taken as 1.44A, then $C_1-O_1^1=1.22$A and $C_1-O_1^2=1.07$A. In the structure shown in Figs. 3 and 4 the carbon-carbon bond makes an angle of 22°21′ with the b axis. In a given carboxyl group $\measuredangle O^1CO^2=117°31'$, $\measuredangle CCO^1=113°50'$ and $\measuredangle CCO^2=102°20'$. The latter angle is perhaps too small. Decreasing the z parameter and increasing the x parameter of carbon will increase the $\measuredangle CCO^2$ and decrease $\measuredangle CCO^1$. Simultaneously the $C-O^1$ distance will be increased, the $C-O^2$ distance decreased, and the carbon atom displaced from the peak of the maximum in the xz projection of Fig. 1. There is considerable uncertainty in the geometry of the oxalate groups because of the uncertainty in the posi-

[12] L. Pauling and M. L. Huggins, Zeits. f. Krist. **87**, 205 (1934).

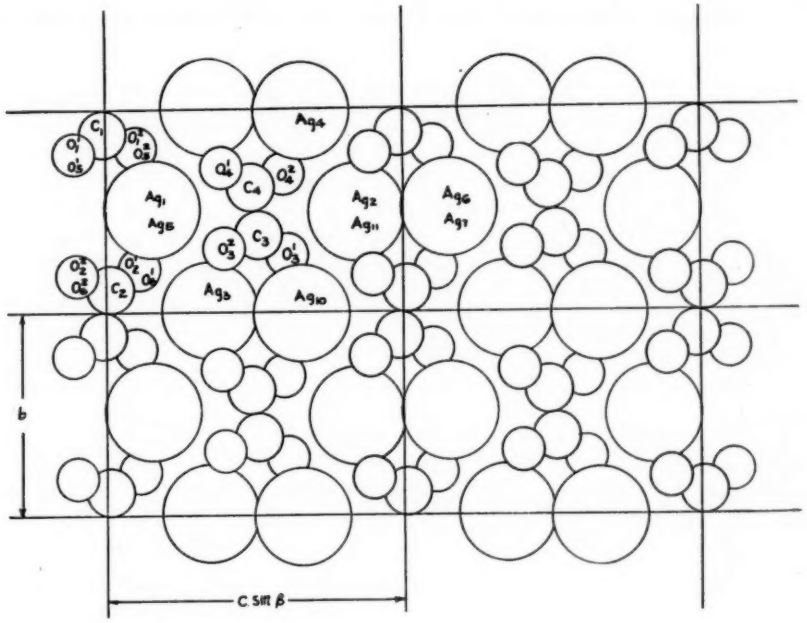

FIG. 4.

tions of the carbon and oxygen atoms, especially the carbon atoms.

The silver oxalate lattice may be considered to be made up of chain molecules, of composition $(Ag_2C_2O_4)_x$, extending through the crystal parallel to the b axis, each unit cell containing two chains passing through the points 000 or 00 1/2. The oxalate groups are bound together to form chains by means of the short Ag−O bonds of length 2.17A and 2.30A. The chains of silver oxalate are then joined together, by means of the Ag−O bonds of length 2.58A and 2.61A, to form sheets of silver oxalate parallel to (100). These sheets of silver oxalate are held together by the longer Ag−O oxygen bonds of length 2.93A and 3.00A. One might expect rather easy cleavage of the 2.93 and 3.00A Ag−O bonds producing a cleavage plane parallel to (100) and perhaps also a cleavage parallel to (001) produced by breaking the Ag−O bonds of 2.6A length. These cleavage planes would intersect at 76° and their possible presence is in agreement with the experimental findings quoted by Macdonald.[6]

It is also of interest to note that structure I contains layers of silver atoms parallel to the (102) planes. One such layer contains silver atoms 3, 4, and 5, in Fig. 3. The centers of the silver atoms are displaced alternately, first to one side and then to the other of the median plane of the layer, the displacement being about 0.2A. Parallel to and lying halfway between the layers of silver atoms are layers of oxalate groups. In a given layer of silver atoms there are strings of close silver atoms extending through the lattice. In Figs. 3 and 4, silver atoms 5, 3, 10, and 11 form part of one chain. The distance Ag_5-Ag_3 is 3.58A and that of Ag_3-Ag_{10} is 3.55A. The smallest Ag−Ag distance in metallic silver is 2.88A.

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The Kinetics of the Oxidation of Isopropyl Alcohol by Chromic Acid

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(Received August 14, 1943)

The oxidation of isopropyl alcohol by chromic acid is a reaction first order with respect to the acid chromate ion, $HCrO_4^-$, first order with respect to the alcohol, and second order with respect to hydrogen ion. Evidence has been obtained that the reaction proceeds by way of a compound of tetravalent or of pentavalent chromium. On the basis of these facts, a mechanism for the oxidation has tentatively been suggested.

I.

THE present investigation was undertaken with the object of determining some of the facts upon which to base a detailed mechanism for the reaction of organic substances with chromic acid. There have been numerous previous studies of such reactions,[1] but most of them have been made without adequate consideration of the role of the acid "catalyst," and without regard for the necessity of maintaining constant ionic strength throughout the reaction. Moreover, in no previous kinetic investigation has the equilibrium

$$Cr_2O_7^{--}+H_2O\rightleftharpoons 2HCrO_4^- \qquad (1)$$

(which occurs in aqueous solutions of chromic acid) been taken into account.

Isopropyl alcohol was chosen for the present study because this compound is water soluble, is oxidized at a convenient rate to a product (acetone) which is stable under the experimental conditions here employed. The data obtained in this study proved sufficient to identify the reactants which form the activated complex; on the basis of this and other information, a possible mechanism for the oxidation reaction has been proposed.

The reaction was carried out at 40° in aqueous solutions and at an ionic strength of 0.400. The oxidation rate was measured by withdrawing aliquot portions of the reaction mixture from time to time and titrating the unreacted chromic acid in these samples iodometrically.

II.

The first step in the kinetic investigation was to determine whether the reaction in question was affected by unusual catalysts which might complicate the detailed study. Hydrochloric, perchloric, and benzenesulfonic acids (all of which are strong monobasic acids) were considered as sources of hydrogen ions. The reaction rates obtained with benzenesulfonic and with perchloric acids were identical; furthermore, perchloric acid in no way interfered with the iodometric titration. When hydrochloric acid was used, however, the rate was about thirty percent lower; and therefore chloride ion was avoided in subsequent work. Intense visible light did not alter the reaction rate. Low concentrations of chromic, ferric, and aluminum ions were also without effect, but manganous ion reduced the rate about fifty percent. In the experiments where this ion was present, a dark brown precipitate of manganese dioxide was formed at one stage of the oxidation; this precipitate, however, redissolved as the reaction approached completion. The significance of these phenomena will be discussed later.

In most of the rate determinations, the concentrations of alcohol and of acid were at least twenty times that of the chromic acid. These conditions were adopted in order to facilitate

[1] (a) C. Jablczynski, Zeits. f. anorg. allgem. Chemie **60**, 38 (1908); (b) R. E. De Lury, J. Phys. Chem. **11**, 47 (1907); (c) N. R. Dahr, J. Chem. Soc. **111**, 707 (1907); (d) A. Kurtenacker, Chem. Abs. **16**, 3421 (1922); (e) J. Piccard and F. de Montmollin, Helv. chim. Acta, **6**, 1021 (1923); (f) B. V. Tronov, V. F. Udodov, and M. I. Chizhova, Zentralblatt **28I**, 2924 (1928); (g) G. Lejeune, J. chim. phys. **24**, 391 (1927); (h) C. Wagner, Zeits. f. anorg. allgem. Chemie **168**, 279 (1928); (i) R. F. Beard and N. W. Taylor, J. Am. Chem. Soc. **51**, 1973 (1929); (j) G. Vavon and C. Zaremba, Bull. soc. chim. [4] **49**, 1853 (1931); (k) V. Majer and V. Marecek, Zeits. f. physik. Chemie **A159**, 181 (1932); (l) H. C. S. Snethlage, Rec. trav. chim. **60**, 199 (1941); (m) H. Amann-Brass, Chem. Abs. **32**, 423 (1938); (n) R. Lang, Mikrochem. Acta **3**, 113 (1938); (o) L. J. Heidt, J. Am. Chem. Soc. **61**, 3455 (1939); (p) E. Lucchi, Chem. Abs. **36**, 6880 (1942).

the separation of the effects of the three different reactants on the rate. As a first approximation, the concentrations of alcohol and acid were constant during any one determination. In successive experiments, the initial concentration of each one of the reactants was varied independently; the change in rate thus observed was attributed to the change in the concentration of this one component.

Preliminary experiments indicated that the oxidation in question is of the fourth order; first order with respect to alcohol, first order with respect to chromic acid, and second order with respect to hydrogen ion. Tentatively, then, the value of the fourth-order constant was determined in accordance with Eqs. (2) and (3).

$$-d(CrO_3)/dt = k(CrO_3)(CH_3CHOHCH_3)(H^+)^2 \quad (2)$$

and

$$kt = \int_{(CrO_3)_0}^{(CrO_3)_t} \frac{-d(CrO_3)}{(CrO_3)(CH_3CHOHCH_3)(H^+)^2} \quad (3)$$

where $(CrO_3)_0$ and $(CrO_3)_t$ are, respectively, the initial concentration of chromic acid (as determined by the iodometric titration) and its concentration at time t.

The integral in Eq. (3) is evaluated in Section V of the present paper. It is important to note that, if the reaction in question is first order with respect to chromic acid, a straight line of slope k should be obtained by plotting the value of the integral against time. If, during a series of experiments, the concentrations of alcohol and acid are kept essentially unchanged, the same value of k should be found for all the experiments of the series, irrespective of the choice of exponents for the terms involving alcohol and hydrogen ion.

In one such series of experiments the initial concentrations of alcohol and acid were 0.2001 molar and 0.2694 molar, respectively, while the initial concentration of chromic acid was varied eighty-fold. For each individual experiment, the value of the integral of Eq. (3), plotted against time is presented in Fig. 1. The agreement with Eq. (3) is satisfactory when the chromic acid concentration is varied from 0.00053 molar to 0.0043 molar. But with higher concentrations of chromic acid, the rate "constant" falls, and with each increase in chromic acid a line of greater curvature is obtained.

The dependence of the rate "constant" on the concentration of chromic acid can be correlated with the equilibrium (1) between the dichromate ion and the acid chromate ion.[2,3] From this equation, it is clear that the proportion of the chromic acid present in the form of acid chromate ion increases as the solution is diluted. The

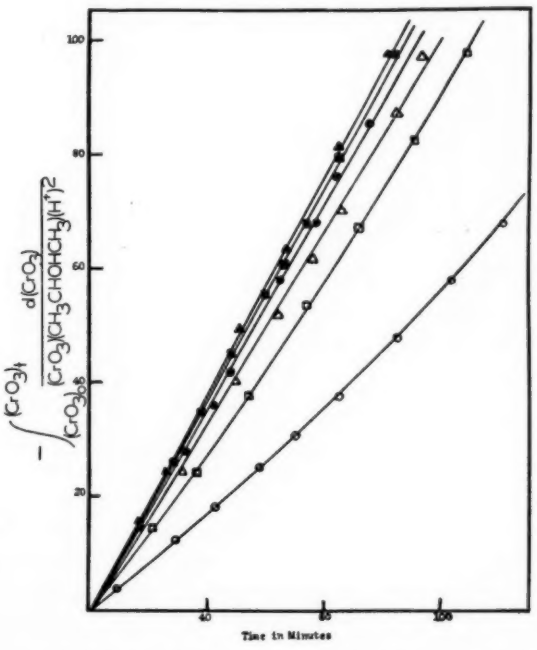


FIG. 1. Graphical representation of Eq. (3) (cf. Eq. (12)). Concentrations of H^+ and $CH_3CHOHCH_3$ were 0.2694 molar and 0.2001 molar, respectively. The various chromic acid concentrations are represented by the following symbols:

○ = 0.04316	△ = 0.004316	■ = 0.001079
□ = 0.01079	● = 0.002158	▲ = 0.0005316.

fact that, in the reaction under consideration, the rate constant is greatest in the dilute solutions where the $HCrO_4^-$ ion predominates suggests that the acid chromate ion is very much

[2] (a) M. S. Sherrill, J. Am. Chem. Soc. **29**, 1641 (1907); (b) R. N. J. Saal, Rec. trav. chim **47**, 73, 264 (1928); (c) J. D. Neuss and W. Rieman, J. Am. Chem. Soc. **56**, 2238 (1934); (d) J. M. Wilson, R. H. Stokes and R. A. Robinson, Trans. Faraday Soc. **37**, 566 (1941).

[3] It is not necessary to consider the ion $HCr_2O_7^-$, since it has been found by a spectrophotometric method that the second ionization constant of dichromic acid is large. Unpublished work and dissertation (Chicago, 1940) of I. M. Klotz.

more important than the dichromate ion in the oxidation.

Further evidence that the acid chromate ion is the principal oxidizing agent is found in the curvature of those lines in Fig. 1 which correspond to experiments where relatively concentrated solutions of chromic acid were used. For the argument which follows, it is necessary to know the approximate value of the concentration of acid chromate ion in solutions containing various concentrations of chromic acid. Several values of the thermodynamic equilibrium constant

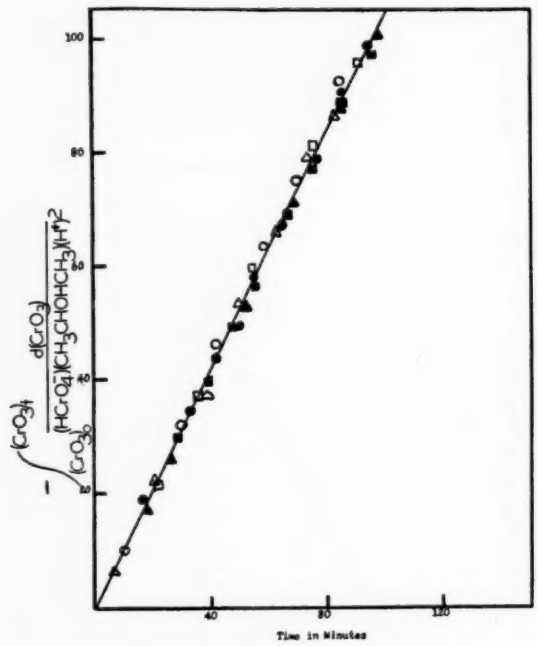


FIG. 2. Graphical representation of Eq. (7) (Cf. Eq. (14)) for the same data shown in Fig. 1.

$$[HCrO_4^-]^2/[Cr_2O_7^{--}] = K \qquad (4)$$

are to be found in the literature;[2] the correct value of 25° is probably about 0.023.[2c] The value for the constant, in terms of concentrations, at an ionic strength of 0.400 and at 40° is not known. A reasonable estimate for this "concentration constant" is 0.015

$$(HCrO_4^-)^2/(Cr_2O_7) = K' = 0.015 \text{ mole/liter.} \qquad (5)$$

(In Eqs. (4) and (5), square brackets represent activities, whereas parentheses are used for concentrations.) A calculation using this latter value for the constant shows that, in an experiment starting with 0.043 molar chromic acid, the acid chromate ion concentration changes, during the first half-life period of the reaction, from thirty-four to forty-five percent of the total chromic acid present. On the other hand, in an experiment starting with 0.00053 molar chromic acid, the acid chromate ion concentration changes during the first half-life period, only from ninety-four to ninety-six percent of the total chromic acid present. Assuming that the acid chromate ion is the principal oxidizing agent, the experiment where 0.00053 molar chromic acid was used should show the largest rate constant, and for this experiment, the graph of the integral in Eq. (3) against time should be essentially a straight line. On the other hand, the experiment where 0.043 molar chromic acid was used should show a much lower rate "constant," and the value of this "constant" should increase as the reaction proceeds. These predictions agree exactly with the experimental findings. Moreover, the suggested hypothesis explains the rising values of rate constants reported by earlier workers.[1j]

The qualitative picture so far presented can be supplemented by a more quantitative argument. If the acid chromate ion is the principal oxidizing agent, the rate equation becomes

TABLE I. Rate of oxidation of isopropyl alcohol. $(H^+) = 0.2694$. $(CH_3CHOHCH_3) = 0.2001$. $K' = 0.015$ mole/liter.

(CrO_3) initial, m/l	k, $(m/l)^{-2}$ min^{-1}
0.04316	2.25
.01079	2.10
.004316	2.05
.002158	2.03
.001079	2.06
.0005316	2.02

$$-d(CrO_3)/dt = k(HCrO_4^-)(CH_3CHOHCH_3)(H^+)^2 \qquad (6)$$

and

$$\int_{(CrO_3)_0}^{(CrO_3)_t} \frac{-d(CrO_3)}{(HCrO_4^-)(CH_3CHOHCH_3)(H^+)^2} = kt. \qquad (7)$$

The concentration of acid chromate ion at any time can be estimated by using the value of 0.015 mole/liter for the concentration constant, K'; while the absolute value of k depends somewhat on the value of K' chosen, it is fortunate that the conclusions which can be derived from the computation do not depend on the value of K' provided that it lies between 0.010 and 0.020.

The integral of Eq. (7) is evaluated in Section V. When the values of this integral are plotted against time, all the points for all the experiments lie essentially on a single straight line. (See Fig. 2.) The values of the fourth-order rate constant are given in Table I. From the satisfactory agreement between prediction and experiment thus shown throughout an eighty-fold range in chromic acid concentration, it is concluded that the oxidation is first order with respect to acid chromate ion.

After it had been shown that the oxidizing agent is acid chromate ion, a series of experiments was carried out in which the initial concentration of isopropyl alcohol was varied over a twenty-fold range. In all of these experiments, the initial concentrations of chromic acid and of hydrogen ion were kept constant; in all instances the concentrations of acid and of alcohol were large compared with that of chromic acid. The results of these experiments are presented in Table II.

Since the rate constant is practically independent of the concentration of isopropyl alcohol, the reaction is evidently first order with respect to this component. The slight increase in rate

TABLE II. The rate of oxidation of isopropyl alcohol. $(H^+) = 0.2694$ m/l. $(CrO_3) = 0.002158$ m/l.

$(CH_3CHOHCH_3)$, m/l	k, $(m/l)^{-3}$ min.$^{-1}$
0.02001	1.90
.04002	1.90
.08004	1.96
.2001	2.03
.4002	2.21

constant with increase in alcohol concentration may be due to a solvent effect. The most concentrated solution listed in Table II contains two percent of isopropyl alcohol. In reactions between oppositely charged ions, an increase in rate with decreasing dielectric constant is quite common.[4]

A method similar to the one just described was used to find the kinetic order of the oxidation with respect to hydrogen ions. The variation in reaction rate when the hydrogen ion concentration was varied twelve-fold corresponds to a rate expression of 1.87 order with respect to hydrogen ion. Apparently the principal reaction with respect to this ion is second order, but in very dilute acid a reaction of first order becomes appreciable. The data are summarized in Table III.

TABLE III. The rate of oxidation of isopropyl alcohol. $(CrO_3) = 0.001079$ m/l. $(CH_3CHOHCH_3) = 0.2001$ m/l.

(H^+), m/l	k, $(m/l)^{-3}$ min.$^{-1}$
0.4000	2.04
.2694	2.06
.1200	2.30
.05280	2.90
.03200	3.60

III.

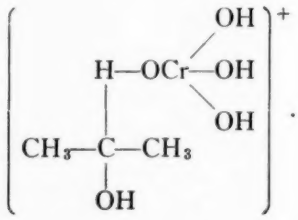
The results hitherto described show that the rate determining step in the oxidation of isopropyl alcohol involves one molecule of alcohol, one of acid chromate ion, and two hydrogen ions. Two types of reactions products are then possible. The reaction may involve a one-electron transfer, in which case the products would be a ketyl free radical and a compound of pentavalent chromium. Alternatively, the reaction may involve a two-electron change, in which case the products would be acetone and a compound of tetravalent chromium. Besides the kinetic support for mechanisms of this type, further evidence has been found for the existence of an intermediate in the reaction containing chromium with a valence greater than three but less than six.

It has been mentioned that manganese dioxide is formed when the reaction in question is carried out in the presence of manganous ion. Chromic acid in acid solution, or in acid solution containing acetone and a chromic salt, does not oxidize manganous ion to manganese dioxide. Therefore, it must be concluded that some inter-

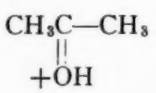
[4] G. Scatchard, J. Chem. Phys. 7, 657 (1939).

mediate, capable of oxidizing manganous ion, is formed during the oxidation of isopropyl alcohol by chromic acid. An unstable compound of pentavalent or tetravalent chromium might well be such an intermediate. Similar evidence for the existence of chromium with a valence of four or five has been presented by other investigators.[1h, m, n, 5]

No conclusive choice of a mechanism for the reaction can be made from the data obtained to date. Tentatively, however, it may be worth while to call attention to a simple picture for an ionic mechanism which fits all the facts known at the present time. If the hydrogen ions involved in the reaction are attached to the oxygen atoms of the acid chromate ion, it should facilitate the removal of a hydrogen atom with an electron pair from the alcohol molecule. The activated complex would then probably have the structure



This compound would then decompose to form the oxonium ion of acetone,



and a compound of tetravalent chromium. An alternative mechanism would involve primary attack upon the hydrogen atom of the alcoholic hydroxyl group.

IV.

Materials

The chromic acid used was prepared by the method of Archibald.[6] The isopropyl alcohol, after being dried and distilled, had a density of 0.7840 25°/4° and an index of refraction, $n_D^{25°} = 1.3758$.[7] The perchloric acid used was Baker's reagent grade. Eastman's benzene sulfonic acid was converted to its barium salt, which was then recrystallized from water. The salt was reconverted to the acid with sulfuric acid, and the resultant solution standardized. G. F. Smith's sodium perchlorate hydrate was recrystallized twice from water; Eastman's sodium benzene sulfonate was purified in a similar manner. All acid solutions were carefully standardized against carbonate free base. The chromic acid was standardized against thiosulfate iodometrically.

Technique

The technique of the rate study was essentially that previously used in this laboratory.[8] The reaction mixtures were brought to an ionic strength of 0.400 by adding sodium perchlorate in those experiments where perchloric acid was used, and by adding sodium benzenesulfonate where benzenesulfonic acid was used. In computing the initial ionic strength, the equilibrium between dichromate ion and acid chromate ion was taken into account. The total concentration of chromic acid was usually small, so the ionic strength did not change appreciably during the course of an experiment. The concentration of acid was computed as the sum of the concentration of chromic acid and that of the added perchloric or benzenesulfonic acid.

The thermostat was constant at a temperature of 39.92°±0.02°. The reaction mixture, except for the alcohol was brought to the temperature of the bath. Then the reaction was initiated by introducing an aliquot of a standard solution of isopropyl alcohol at 40°.

Completeness of the Reaction

Fifty cc of 1.190N perchloric acid, 25 cc of 2.001M isopropyl alcohol and 25 cc of 0.1079M chromic acid were added to a 250-cc volumetric flask, and the mixture made up to volume. This solution was allowed to stand for 48 hours at 40°, and then analyzed for acetone by the method

[5] V. F. Stefanovskii and A. M. Zanko, Acta. Physiochim. U.S.S.R. **9**, 635 (1938).

[6] E. H. Archibald, *The Preparation of Pure Inorganic Substances* (J. Wiley and Sons, New York, 1932), pp. 279.

[7] A. Weissberger and E. Proskauer, *Organic Solvents* (Oxford University Press, Oxford, 1935), pp. 27.

[8] F. H. Westheimer and R. P. Metcalf, J. Am. Chem. Soc. **63**, 1339 (1941).

of Iddles and Jackson.[9] This method involves the precipitation of the 2,4-dinitrophenylhydrazone of acetone. In one experiment, a 97.9 percent yield of hydrazone, melting at 124.5–125° before recrystallization, was obtained. In blank experiments on pure acetone, 96–98 percent yields of the hydrazone were obtained; these samples, when recrystallized, melted at 126°.

Effect of Light

An experiment was made with 0.01079 molar chromic acid, 0.2001 molar isopropyl alcohol and 0.2694 molar hydrogen ion. The reaction was first conducted in the dark; then a duplicate experiment was carried out with the Pyrex reaction flask 30 cm from a 250-watt lamp.

Catalytic Effects

Experiments were made with 0.01079 molar chromic acid, 0.2001 molar isopropyl alcohol and 0.02694 molar hydrogen ion, in the presence of 0.0008 molar chromic, ferric, aluminum and manganous ions.

Identification of Manganese Dioxide

A solution consisting of 20 cc of 1.079 molar chromic acid, 15 cc of 2.001 molar isopropyl alcohol, 25 cc of 0.020 molar manganese chloride and 40 cc of 1.190 molar perchloric acid was kept at 40° for an hour. The precipitate which formed during this time separated by filtration, washed first with water, then with acetone, and finally dried at 110° for 24 hours. Qualitative analysis showed that manganese was the only cation present. The quantitative analysis for manganese dioxide was carried out by the method of Mellor.[10] The precipitate in question had an oxidizing value corresponding to 82.4 percent MnO_2. It might then contain 1.03 molecules of water for each molecule of oxide. Since manganese dioxide is known to form various indeterminate hydrates, this finding is reasonable. The result was confirmed by an independent analysis for manganese in which the bismuthate method of Hillebrand and Lundell was used.[11]

V.

The stoichiometry for the oxidation of isopropyl alcohol by chromic acid in acid solution can be expressed by the pair of equations

$$Cr_2O_7^{--}+3CH_3CHOHCH_3+8H^+\rightarrow 2Cr^{+++}+3CH_3COCH_3+7H_2O \quad (8)$$

and

$$2HCrO_4^-+3CH_3CHOHCH_3+8H^+\rightarrow 2Cr^{+++}+3CH_3CHOHCH_3+8H_2O. \quad (9)$$

Evidently, the ratios of hexavalent chromium to acid and to alcohol are identical in Eqs. (8) and (9).

The simple fourth-order rate equation is

$$-(CrO_3)/dt = k(CrO_3)(CH_3CHOHCH_3)(H^+)^2. \quad (2)$$

This equation by substitution becomes

$$+dx/dt = k(b'-x)(a'-3x/2)(c'-4x)^2 \quad (10)$$

where a' = initial concentration of isopropyl alcohol in moles/liter
b' = initial concentration of chromic acid in moles/liter
c' = initial concentration of hydrogen ion in moles/liter
x = concentration of chromic ion, in moles/liter, at time t.

A simple algebraic transformation leads to

$$dx/dt = 24k(b-x)(a-x)(c-x)^2$$

where

$$a = 2a'/3$$
$$b = b'$$
$$c = c'/4.$$

Integration of this equation leads to the expression

$$J \ln a/(a-x)+K \ln b/(b-x) +M \ln c/(c-x)+Lx/c(c-x)=24kt \quad (12)$$

where

$$J = 1(b-a)(c-a)^2$$
$$K = 1/(a-b)(c-b)^2$$
$$L = 1/(c-a)(c-b)$$
$$M = (2c-b-a)/(c-a)^2(c-b)^2.$$

[9] H. A. Iddles and C. E. Jackson, Ind. Eng. Chem. Anal. Ed. **6**, 454 (1934).
[10] J. W. Mellor and H. V. Thompson, *Quantitative Inorganic Analysis*, (C. Griffin and Company, London, 1938), p. 404.
[11] W. E. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis* (J. Wiley and Company, New York, 1929), p. 346.

Equation (12) was used to find the curves shown in Fig. 1.

The rate expression involving the acid chromate ion is

$$-d(CrO_3)/dt = k(HCrO_4^-)(CH_3CHOHCH_3)(H^+)^2. \quad (6)$$

The concentration of acid chromate ion can be calculated from the equilibrium expression

$$K' = (HCrO_4^-)^2/(Cr_2O_7^{--}) = 0.015 \text{ mole/liter} \quad (5)$$

where the parentheses indicate concentrations, not activities. Using the notation defined above,

$$(HCrO_4^-) = \frac{-K' + [K'^2 + 8K'(b-x)]^{\frac{1}{2}}}{4}. \quad (13)$$

The integrated rate equation becomes

$$\frac{1}{6}\int_0^x \frac{dx}{(a-x)(c-x)^2[-K' + K'^2 + 8K'(b-x)]^{\frac{1}{2}}} = kt. \quad (14)$$

The indicated integration was performed graphically.

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Statistical Mechanics of Cross-Linked Polymer Networks

I. Rubberlike Elasticity[1]

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(Received October 4, 1943)

A model is proposed for the structure of a cross-linked network, such as exists in a vulcanized rubber, which is amenable to statistical treatment. Expressions are derived for the structural entropy of the network, and for the entropy change on deformation. The latter is in agreement with the relationship derived by Wall and others by a different treatment.

IT has been adequately demonstrated that the elastic retractive forces in rubber and rubberlike materials arise principally from the decrease in entropy accompanying deformation.[2,3] Only at high degrees of elongation, where crystallization may occur to a considerable degree, does the term $(\partial\Delta H/\partial L)_T$ assume a magnitude comparable with $T(\partial\Delta S/\partial L)_T$, L being the length of the sample in the direction of stretch. Hence, to an approximation which is good except for large deformations the retractive force is given by

$$f = (\partial\Delta F/\partial L)_T \cong -T(\partial\Delta S/\partial L)_T. \quad (1)$$

From the standpoint of polymer structure, a vulcanized rubber consists of a three-dimensional network composed of very long rubber molecules laterally attached to one another at occasional points along their lengths. The cross-linkages may consist of primary valence bonds connecting the chains directly, or of an intermediate group or atom such as sulfur which is bonded to each of the two chains. The precise nature of the cross-linkage is relatively unimportant here, aside from the stipulation that it be of a permanent nature. In the course of the cross-linking process (vulcanization) the original long polymer molecules can be considered to lose their identity, and there emerges a single giant network structure, the basic elements of which are the portions of the molecules reaching from one cross-linkage to the next. This basic element will be called a chain. (The term "chain" will not be applied to the long polymer molecules from which the network is formed.)

[1] A preliminary account of the work presented in this and the following paper was presented before the New York Academy of Sciences Conference on High Polymers, January 9, 1943.

[2] K. H. Meyer and C. Ferri, Helv. Chim. Acta **18**, 570 (1935); D. S. Ornstein, J. Wouda, and J. G. Eymers, Proc. Akad. Wetensch. Amst. **33**, 273 (1930); V. Hauk and W. Neumann, Zeits. f. physik. Chemie **A182**, 285 (1938); E. Guth, J. Phys. Chem. **46**, 826 (1942).

[3] L. R. G. Treloar, Trans. Faraday Soc. **38**, 293 (1942).

The cross-linkages bestow a degree of permanence on the network structure; the midportion of a chain is free to assume many configurations, but each end of the chain is constrained to join the ends of three other chains at the cross-linkage. When deformation occurs, the cross-linkages are shifted to new positions relative to one another in a manner paralleling the macroscopic deformation. Consequently the "displacement lengths" of the chains, i.e., the lengths of the vectors connecting the ends of the chains, are altered from their equilibrium distribution in the undeformed state. Since it may be assumed that the chains occupy most probable configurations in the undeformed state, deformation of the network forces them to assume less probable configurations; hence, the entropy decreases with deformation.[4]

Quantitative treatments of this problem have been based on the following expression derived by Guth and Mark[5] and by Kuhn[6] for the probability of a displacement length r.

$$W(r)dr=(4\beta^3/\pi^{\frac{1}{2}})\exp(-\beta^2r^2)r^2dr. \quad (2)$$

Or, expressing r in rectangular coordinates

$$W(xyz)dxdydz=(\beta^3/\pi^{\frac{3}{2}})\times\exp[-\beta^2(x^2+y^2+z^2)]dxdydz. \quad (2')$$

β, the reciprocal of the most probable value of r, is dependent upon the contour length of the chain and its flexibility. If the chain possesses bonds about which there is only limited rotation, restricted perhaps by sterically interfering substituents, Kuhn has pointed out that its configurations in space may be replaced approximately by those assumed by a chain of the same contour length having a fewer number of bonds about which rotation is unhindered. These bonds will occur at correspondingly greater intervals along this chain of equivalent flexibility. For a chain containing Z bonds located at intervals of length l along the chain, successive segments of which meet at tetrahedral angles[5-7]

$$\beta^2=3/4Zl^2. \quad (3)$$

In deriving the modulus of elasticity of a rubber from (2), Kuhn[8] introduced the fundamental assumption that the deformation transforms the chain displacement lengths like macroscopic elements of a homogeneous isotropic medium. Thus, elongation of the sample in the z direction to a relative length α times the initial length is assumed to increase the z component of the chain displacement vector $\mathbf{r}$ (which connects one end of the chain with the other) by the factor α; since there is no appreciable change in volume, the x and y components are assumed to be decreased by the factor $1/\alpha^{\frac{1}{2}}$. Kuhn proceeded to apply his treatment to a system of independent molecular units whose dimensions were presumed to be restricted not only in the direction of r, but in the directions perpendicular to r, as well. He obtained for the modulus of elasticity at small deformations

$$\epsilon=7(\nu/V)kT,$$

where ν is the number of chains in the volume V. Recognition of the fact that in the network structure of a vulcanized rubber the "molecular unit" is the chain discussed above, and that only the ends of the chains are subject to constraints which depend on the degree of deformation, leads by the same procedure to

$$\epsilon=3(\nu/V)kT=3RT\rho/M_c, \quad (4)$$

where ρ is the density of rubber and M_c is the molecular weight of the chain.

Recently Wall[9] has shown by an improved mathematical treatment, based on Kuhn's fundamental assumption stated above, that the retractive force at any elongation is given by

$$f=(RTA_0\rho/M_c)(\alpha-1/\alpha^2), \quad (5)$$

where A_0 is the initial cross-sectional area. Or, for the modulus of elasticity

$$\epsilon=(RT\rho/M_c)(1+2/\alpha^3), \quad (6)$$

which reduces to (4) for small deformations. These same equations have been derived by Treloar[10] by an accurate reduction of Kuhn's equations.[11]

[4] K. H. Meyer, G. von Susich, and E. Valko, Kolloid Zeits. **59**, 208 (1932).
[5] E. Guth and H. Mark, Monats. **65**, 63 (1934).
[6] W. Kuhn, Kolloid Zeits. **68**, 2 (1934).
[7] H. Eyring, Phys. Rev. **39**, 746 (1932).
[8] W. Kuhn, Kolloid Zeits. **76**, 258 (1936).
[9] F. T. Wall, J. Chem. Phys. **10**, 485 (1942).
[10] L. R. G. Treloar, Trans. Faraday Soc. **39**, 36 (1943).
[11] Similar relationships have been derived by Guth and James. Full details of their treatment have only appeared

In postulating that the distribution of chain displacement lengths is transformed by the deformation in the simple manner assumed in the Kuhn-Wall treatment, the chains are treated essentially as independent elements transformed by the deformation. The interdependence of mutually connected chains is not specifically taken into account. In the treatment which we present here the introduction of an idealized network model obviates the basic assumption employed by Kuhn and Wall concerning the transformation of the chain displacement lengths during deformation. While we do not suggest that our treatment of deformations is preferable to those discussed above, it offers certain advantages in the treatment of swelling phenomena discussed in the following paper.[12]

THE MODEL AND ASSOCIATED ASSUMPTIONS

We consider a process whereby a three-dimensional network structure is formed by the introduction of occasional cross-linkages between very long polymer molecules. If, as ordinarily will be the case, the cross-linkages are introduced at random into the mass of randomly entangled molecules the distribution of chain contour lengths will be given by[13]

$$N_i = Np(1-p)^{i-1}, \qquad (7)$$

the chain element of the network being defined as above. Here N_i is the number of chains composed of i units, N is the total number of chains in the network, and p is the probability that any particular chain unit (e.g., C_5H_8 in rubber) is cross-linked.

It can be imagined that the points at which cross-linking is destined to occur have been labeled before vulcanization. The chains so defined are free to assume any physically accessible configuration. Not only will the contour lengths i of the chains vary, in accordance with (7), but their displacement lengths r will exhibit further variation. The displacement lengths of chains containing i units will be distributed about a root-mean-square r value in the manner described by Eq. (2). If we imagine that the cross-linkages are introduced instantaneously at the labeled points, the chain irregularity existing before cross-linking will be carried over into the network structure. The important difference between the vulcanized and the unvulcanized states may be set forth as follows. Each chain, which prior to vulcanization is designated as the molecular portion between two labeled points, can be characterized by the vector $\mathbf{r}$ leading from one end of the chain to the other. Before vulcanization these vectors are entirely independent of one another; the directions they may assume are unrestricted and their lengths are independently distributed according to Eq. (1). After vulcanization, neither the length nor the direction of one of these vectors can be altered without affecting adjacently connected vectors.

In the analysis presented here, attention is focused on the points of cross-linkage rather than on the chains themselves. The cross-linkages may be regarded as centers of tetrafunctionality since the ends of four chains meet at each of these points. Surrounding a given cross-linkage there are four "nearest neighbor" cross-linkages at the other ends of the four chains meeting at the given central cross-linkage. These "nearest neighbor" cross-linkages will not, in general, be nearest in space; they are the nearest only with reference to the continuous network structure. The cross-linkages are not bound to fixed positions; they may diffuse through limited regions of the space. This is a consequence of the multiplicity of configurations which each chain may assume through bond rotations. However, displacements of the order of magnitude of the mean chain displacement length or greater are very improbable. They can be achieved only by imposing highly improbable displacement lengths on a few of the neighboring chains of the network, or by imposing slightly improbable displacement lengths on a great many chains including those more distantly removed. Thus, most probable configurations may be assigned to the nearest neighbor cross-linkages about a given cross-linkage. These four points will lie at the corners of a tetrahedron, which will be an irregular tetrahedron since the lengths of the four chains will differ.

after submission of this manuscript: H. M. James and E. Guth, J. Chem. Phys. **11**, 455 (1943). See also E. Guth and H. M. James, Ind. Eng. Chem. **33**, 624 (1941); **34**, 1365 (1942).

[12] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. **11**, 521 (1943).

[13] P. J. Flory, J. Am. Chem. Soc. **58**, 1877 (1936).

In the treatment given here we have introduced the following assumptions and approximations:

(1) That the actual network can be replaced by one in which all of the chains are of the same contour length. Under this assumption, the most probable positions for the junctions surrounding a given cross-linkage may be assumed *on the average* to lie at the corners of a regular tetrahedron.

(2) That the properties of the network can be computed from those of this average "cell."

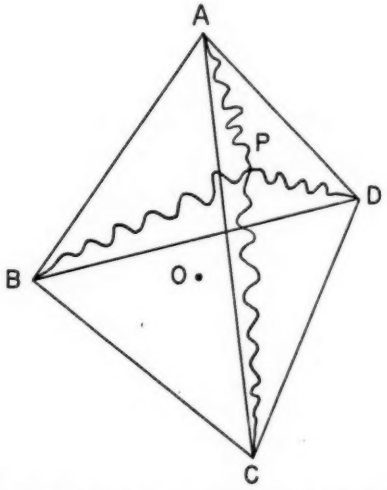

FIG. 1. Model for the elementary tetrahedral cell of tetrafunctional three-dimensional network.

(3) That the actual restraints imposed by the network on a given cross-linkage can be replaced by those obtained on fixing its nearest neighbor cross-linkages at their most probable average positions, i.e., by fixing the nearest neighbor cross-linkages at the corners of a regular tetrahedron.

(4) Finally, the distribution function [Eq. (2)] is assumed to apply to the independent chains prior to vulcanization. Validity of this assumption requires that the chains be long enough for Eq. (2) to be applicable with sufficient accuracy.

In introducing the concept of a regular tetrahedral "cell" as a representative unit of the network structure, it must be made clear that these cells are not mutually exclusive so far as occupancy of the space is concerned. Various tetrahedra, distantly connected along the network structure, will interpenetrate the same region of space. This interpenetration which, fundamentally, is the result of the random intertwining of the chains must exist to the extent that within a single tetrahedron there will be many cross-linkages belonging to other tetrahedra. Consequently, it is impossible to conceive of a continuous array of regular tetrahedra such as occurs in the diamond lattice. The regular tetrahedral cell is introduced only as an average representative cell.

The average cell is shown in Fig. 1. The most probable positions of the four nearest neighbor cross-linkages lie at the corners A, B, C, and D of the tetrahedron. In accordance with assumption (3) these are considered to be fixed points. The four chains extending from A, B, C, and D to the central junction at P are indicated by wavy lines. (Their actual configurations will be much more irregular than is indicated by these lines.) The point P can occupy numerous positions, but points far from the center O of the tetrahedron can be occupied only by extending some (or all) of the four chains to improbable displacement lengths.

STRUCTURAL ENTROPY OF NETWORK FORMATION

We consider first the process of construction of the idealized network discussed above from ν separate chains, instead of from a number of linear molecules of great length, each of which contains many chains. This process of network formation from separate chains can be divided into two steps represented schematically as follows:

$$(A)\quad \nu \text{ —} + \nu/4 \text{ "cross-linkages"} \rightarrow \nu/4 \;\text{—}\!\!+\!\!\text{—},$$

where each straight line segment represents a chain and ν is the total number of chains. The "nuclei" resulting from step (A) then combine with one another, as indicated in the next step, the additional $\nu/4$ cross-linkages combining the unattached chain ends to form the final network structure.

$$(B)\quad \nu/4 \;\text{—}\!\!+\!\!\text{—} + \nu/4 \text{ "cross-linkages"} \rightarrow \text{final network.}$$

Next we consider the formation, from the chains, of long polymer molecules such as are actually

presumed to be present prior to the introduction of cross-linkages (i.e., prior to vulcanization). This may be represented by

(C) — → —•—•—•—, etc.

The resultant of $(A)+(B)-(C)$ represents the cross-linking process with which we are primarily concerned.

In step (A) three chains are constrained to meet within a volume element $\Delta\tau$ located at the end of a fourth chain. The size of $\Delta\tau$ will be dictated by the chemical structure of the cross-linkage, bond rigidities, etc.; $\Delta\tau$ will be independent of deformation. The probability that the chains group themselves in this manner is

$$[\nu!2^{\nu}/(4!)^{\nu/4}](\Delta\tau/V)^{3\nu/4},$$

where V is the total volume of the system. The factor 2^{ν} is included in consideration of the identity of the two ends of each chain.

Step (A) requires also that the $\nu/4$ cross-linkages be arranged in the vicinity of "lattice points" corresponding to the corners of the ultimate tetrahedral "cells" of the network. Hence, the additional factor $(\Delta\tau'/V)^{\nu/4}$ is required, where $\Delta\tau'$ is the size of the volume element to which each junction is assigned. Furthermore, in anticipation of step (B), we consider here the degeneracy in the orientations of the group of four chains which meets at each cross-linkage. There are twelve ways in which each of these groups may associate with its four neighboring junctions to be formed in step (B). For the probability of step (A) we write, therefore

$$W_A=\nu!(2\Delta\tau/V)^{3\nu/4}(\Delta\tau'/V)^{\nu/4}. \tag{8}$$

For the entropy change, we obtain upon introducing Stirling's approximations

$$\Delta S_A=k\ln W_A=k\nu[\ln(\nu/V)-1+(3/4)\ln(2\Delta\tau)+(1/4)\ln\Delta\tau']. \tag{9}$$

Having arranged $\nu/4$ cross-linkages at the corners of $\nu/4$ tetrahedral cells, step (B) involves the junction within each tetrahedron of the ends of four chains emanating from the corners of the tetrahedron. The probability that four such chain ends would meet spontaneously within the same volume element $\Delta\tau=dx\,dy\,dz$ ($\Delta\tau$ being defined as above) of an average cell (regular tetrahedron) is

$$\Omega(xyz)(dx\,dy\,dz)^4=\prod_{i=1}^{4}W(x_iy_iz_i)dx_idy_idz_i,$$

where x_i, y_i, z_i, etc., are the coordinates of the same volume element $\Delta\tau$ referred, respectively, to the four corners A, B, C, D, of the tetrahedron (see Fig. 1), and x, y, and z are coordinates of the volume element referred to the center O of the tetrahedron. On substituting for W from Eq. (2′)

$$\Omega(xyz)=(\beta^{12}/\pi^6)\exp[-\beta^2\sum_{i=1}^{4}r_i^2]. \tag{10}$$

In Appendix I it is shown that for the undeformed network, i.e., for a regular tetrahedral "cell"

$$\sum_{i=1}^{4}r_i^2=4(s^2+\lambda^2), \tag{11}$$

where

$$s^2=x^2+y^2+z^2,$$

x, y, and z being referred to O, and λ is the distance AO from the center of the tetrahedron to one corner. The probability that all four chains terminate in the same volume element located *any place* becomes

$$\Omega_0(\Delta\tau)^3=\left[\int_{\tau}\Omega(xyz)\Delta\tau\right](\Delta\tau)^3$$

$$=(4\beta^{12}/\pi^5)\left\{\int_0^{\infty}\exp[-4\beta^2(\lambda^2+s^2)]s^2ds\right\}(\Delta\tau)^3$$

$$=(\beta^9/8\pi^{9/2})\exp(-4\beta^2\lambda^2)(\Delta\tau)^3. \tag{12}$$

Hence, for the entropy change in step (B), involving $\nu/4$ elementary tetrahedra,

$$\Delta S_B=(k\nu/4)[3\ln(\beta^3/2\pi^{\frac{1}{2}})-4\beta^2\lambda^2+3\ln\Delta\tau]. \tag{13}$$

For the third step (C) above, assuming that each polymer molecule contains many chains,

$$W_C\cong\left(\frac{\Delta\tau''}{V}\right)^{\nu}2^{\nu}\nu!$$

$$\Delta S_C\cong k\nu[\ln(2\nu/V)+\ln\Delta\tau''-1]. \tag{14}$$

Finally, for the structural entropy of vulcani-

zation, or cross-linking,

$$\Delta S_v=\Delta S_A+\Delta S_B-\Delta S_C$$
$$=k\nu[\tfrac{3}{4}\ln(\beta^3/\pi^{\frac{3}{2}})-\beta^2\lambda^2+\tfrac{3}{2}\ln\Delta\tau+\tfrac{1}{4}\ln\Delta\tau'-\ln\Delta\tau''-\ln 2]. \quad (15)$$

Both $\Delta\tau$ and $\Delta\tau''$, being determined by the chemical bond structure in the vicinity of the cross-linkage, are independent of network deformations, and we assume that this is true also of $\Delta\tau'$.[13] Consequently, for the purposes of the following development the magnitudes of the $\Delta\tau$'s are of no importance, and we may write

$$\Delta S_v=k\nu[(3/4)\ln(\beta^3/\pi^{\frac{3}{2}})-\beta^2\lambda^2+\text{const.}]. \quad (16)$$

The dimension of the tetrahedron λ is to be taken equal to a mean chain displacement length, since at the instant vulcanization occurs the chains are assumed to exist in random configurations. Within the bounds of our assumptions concerning the representative tetrahedral cell, it is not possible to specify what type of average value of r should be used. If we let $\lambda^2=\overline{r^2}$, then since according to Eq. (2) $\overline{r^2}=3/2\beta^2$, $\beta^2\lambda^2$ can be replaced by $3/2$.

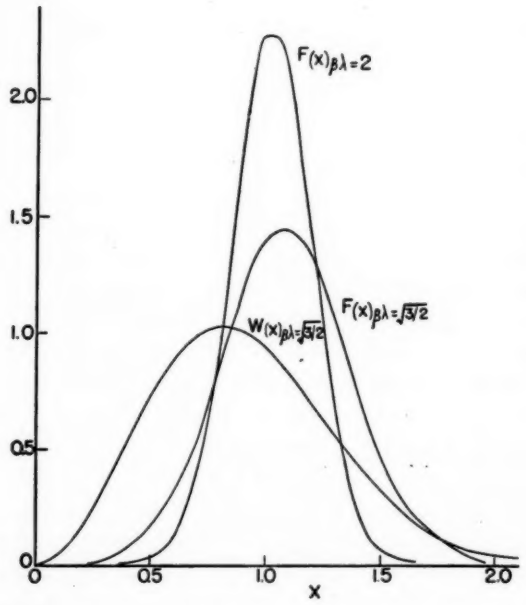

FIG. 2. Comparison of the distributions of chain displacement lengths for isolated chains ($W(x)$) and for the cross-linked state ($F(x)$).

[13] Possible moderate dependence of $\Delta\tau'$ on deformation would have little effect on subsequent results.

ENTROPY OF DEFORMATION

If the vulcanized rubber is deformed by an externally applied stress, the regular tetrahedral array of cross-linkages in the idealized model discussed above will be distorted. In other words, the most probable positions for a given set of four nearest neighbor cross-linkages will no longer lie at the corners of a regular tetrahedron. The manner in which a given tetrahedron is distorted will depend on its orientation with respect to the principal axes of the strain tensor. If, for example, the sample is elongated in a direction parallel to OA in Fig. 1, the tetrahedron will be converted to a regular pyramid, $OA=\lambda$ being transformed to a length $\alpha\lambda$, where α is the ratio of the deformed length to the initial length along the axis of strain. Since the change in density with deformation is negligible for rubber-like materials, except in the region where crystallization occurs, dimensions of the tetrahedron perpendicular to OA will change by the factor $1/\alpha^{\frac{1}{2}}$.

We now proceed to the deduction of the structural entropy of formation of the deformed network. Step (A) will differ only with respect to the spatial distribution of the $\nu/4$ cross-linkages. The entropy change will be the same as was found previously. Step (C) also requires no modification. Step (B) will differ inasmuch as Eq. (11) no longer applies to the deformed tetrahedron.

In place of (11) we should average $\sum r_i^2$ over all orientations of the direction of elongation with respect to the tetrahedron. An integration of this sort has not been carried out. However, it is shown in Appendix I that for orientations of the direction of the strain either perpendicular to or parallel to a face of the tetrahedron

$$\sum_{i=1}^{4} r_i^2=4s^2+4\lambda^2(\alpha^2+2/\alpha)/3. \quad (17)$$

We assume that this equation represents the average resultant for all orientations.

Substitution of (17) in (10) leads ultimately to

$$\Delta S_v=k\nu[(3/4)\ln(\beta^3/\pi^{\frac{3}{2}})-\beta^2\lambda^2(\alpha^2+2/\alpha)/3+\text{const.}] \quad (18)$$

for the entropy of vulcanization. Equation (18) reduces to (16) for the undeformed state $\alpha=1$.

Subtracting (16) from (18) there is obtained for the entropy of deformation

$$\Delta S_d = -k\nu\beta^2\lambda^2(\alpha^2+2/\alpha-3)/3. \qquad (19)$$

If we let $\beta^2\lambda^2=3/2$,

$$\Delta S_d = -k\nu(\alpha^2+2/\alpha-3)/2, \qquad (19')$$

which is identical with Wall's[9] expression for the entropy of deformation. Taking $\Delta H_d=0$ and substituting $T\Delta S_d=-\Delta F$ in Eq. (1), Eqs. (5) and (6) are obtained for the retractive force and for Young's modulus of elasticity, respectively.

DISCUSSION

Both the Kuhn-Wall treatment and the one we have presented depend upon Eq. (2) for the probability distribution of chain lengths. The foundation for this relationship is reasonably secure, aside from the uncertainty in the magnitude of β, which does not enter into the elasticity calculations. The critical assumption involved in our treatment pertains to the use of the regular tetrahedron as a representative cell of the network structure. No specific model for the network is required in the Kuhn-Wall treatment. However, it has been necessary for them to postulate that the distribution of chain lengths is transformed directly as the macroscopic dimensions of the sample. No such postulate enters into our treatment.

It is of interest to inquire into the compatability of this assumption with the restrictions imposed by the network structure, using the model we have assumed. If all cells of the network were regular tetrahedra, the corners of which are fixed with reference to their centers, a condition which goes beyond our actual assumptions,[14] then, as is shown in Appendix II, the distribution of chain lengths becomes

$$F(x) = (4\beta\lambda/\pi^{\frac{1}{2}}) \exp\left[-4\beta^2\lambda^2(1+x^2)\right] \times \sinh(8\beta^2\lambda^2 x)x\,dx, \qquad (20)$$

where $x=r/\lambda$. This function is shown in Fig. 2 in comparison with $W(x)$ according to Eq. (2) for several values of $\beta^2\lambda^2$. The shapes of the distributions given by the two functions differ, $F(x)$ being narrower than $W(x)$. This is due to the ordering resulting from adoption of the regular tetrahedron cell. However, the distribution becomes sharper as $\beta^2\lambda^2$ is increased; i.e., as the tetrahedron is isotropically enlarged. This magnification of the tetrahedron (increase in λ) corresponds to the change in structure resulting from swelling, as discussed in the following paper. We conclude that swelling causes the distribution of chain lengths to become relatively narrower. The assumption made by Kuhn and Wall (for the case of deformations without change in volume) appears to be inapplicable to deformations accompanied by changes in volume.

Our method of treatment permits an estimate of the structural entropy change accompanying network formation from very long molecules which become cross-linked to one another *at specified points of reactivity* along their lengths. The actual magnitude of this entropy change, given by Eq. (15), is indeterminate to the extent of the arbitrariness in the values of the $\Delta\tau$'s. If we assume that each of the $\Delta\tau$'s is approximately equal to the volume of one of the Z chain elements, which will be of the order of l^3, and taking $\beta^2\lambda^2=3/2$,

$$\Delta S_v = -k\nu[(9/8)\ln Z+3.4]. \qquad (21)$$

Or, for the entropy per mole of cross-linkages in the network

$$-R[(9/4)\ln Z+6.8].$$

This entropy term becomes quite large when the lengths of the chain are great.

If the points at which cross-linking may occur cannot be specified in advance, as for example in the vulcanization of natural rubber, these expressions lose their significance. Thus, if cross-linking may occur wherever two molecules are in contact (as would very nearly be the case for natural rubber with its numerous unsaturated linkages), attachment of the chains to one another takes place without imposing on the system an increase in order. Consequently, there will be no structural entropy change. This will not hold true if the material possesses only a few reactive points, all, or nearly all, of which are to be utilized in the formation of cross-linkage. A typical example is found in the vulcanization of Butyl rubber,[15] an olefin-diolefin copolymer

[14] We have assumed only that the *average* cell *is a regular tetrahedron.*

[15] R. M. Thomas, I. E. Lightbown, W. J. Sparks, P. K. Frolich, and E. V. Murphree, Ind. Eng. Chem. **36**, 1283 (1940).

containing only a small proportion of the latter. In such instances Eq. (21) may be presumed to yield a significant estimate of the structural entropy of vulcanization.

We have assumed [assumption (1)] that our idealized network formed from regularly spaced points of cross-linkage will possess the same elastic properties as an actual completely random one. Although the actual magnitude of ΔS_v given by Eq. (15) may be of little or no significance as pointed out above, we assume that the difference between Eqs. (18) and (15) represents correctly the change in entropy due to deformation.

The rather artificial approximations involved in steps (*A*) and (*C*) effectively cancel out in ΔS_d, the entropy of deformation. Only step (*B*) contributes to the terms appearing in the deformation formulas. The equivalence of our results with those of Wall[9] and Treloar,[10] obtained by a fundamentally different procedure, adds considerable support to equations (19), (5), and (6) relating elastic properties to structure.

Similar treatments can be applied to networks in which either three or six chains (instead of four) are joined at the network junction points. For a network containing trifunctional junctions, the elementary cell becomes a triangle (instead of a tetrahedron) the corners of which represent the nearest neighbor junctions with respect to the given central junction. For a hexafunctional network, the elementary cell becomes an octahedron. In both cases the formula for the sum of the squares of the distances from the f neighboring junctions to the central junction located at a distance s from the center of the deformed cell can be expressed

$$\sum_{i=1}^{f} r_i^2 = fs^2 + f\lambda(\alpha^2 + 2/\alpha)/3, \qquad (17')$$

which reduces to Eq. (17) for a tetrafunctional network ($f=4$). Upon carrying through treatments paralleling that given above it is found that the entropy of deformation becomes

$$\Delta S_d = -(k/2)[\nu/(f/2)]\beta^2\lambda^2 \times \left\{\left[\sum_{i=1}^{f} r_i^2\right]_{\alpha} - \left[\sum_{i=1}^{f} r_i^2\right]_{\alpha=1}\right\}.$$

Substitution of the more general expression (17′) into this equation gives Eq. (19) for the entropy of deformation. Since this equation does not contain f, we conclude that only the number of chains and not the functionality of their interconnecting linkages is important. The results which have been obtained therefore should be equally applicable to networks of functionality other than four.

We have been concerned primarily with networks formed by cross-linking of previously formed long molecules. It should be pointed out, however, that simultaneous linear growth and cross-linking or branching may produce equivalent network structures. Typical examples of polymers of this type include the products of copolymerization of a vinyl compound (e.g., styrene) with a small amount of a divinyl substance (e.g., divinyl benzene),[16–18] or of polycondensation of bi- and multifunctional reactants.[19] In order for the above treatment to apply, it is only necessary that the multifunctional linkages be introduced under conditions of random coiling. In any case the polymer must possess sufficient internal mobility to allow the chains to slip past one another during deformation; i.e., the polymer must be at a temperature such that it displays rubber-like behavior, or it must contain a sufficient quantity of a plasticizer to accomplish the same result.

APPENDIX I

Case 1

Consider a regular tetrahedron $ABCD$, as shown in Fig. 3. Let its center 0 be the origin of a set of rectangular coordinates of which the z axis passes through the apex A, the x axis is parallel to the edge BC, and the y axis is parallel to the bisector of the angle BDC. Let r_1, r_2, r_3, and r_4 be the distances from the corners A, D, C, and B, respectively, to a point $P(x, y, z)$ located at a distance s from the origin. Let λ be the distance from the origin to any of the corners. It can then be shown by simple geometry that

$$r_1^2 = s^2 - 2\lambda z + \lambda^2,$$
$$r_2^2 = s^2 - (4\sqrt{2}/3)\lambda y + \tfrac{2}{3}\lambda z + \lambda^2,$$
$$r_3^2 = s^2 - 2(2/3)^{\frac{1}{2}}\lambda x + (2\sqrt{2}/3)\lambda y + \tfrac{2}{3}\lambda z + \lambda^2,$$
$$r_4^2 = s^2 + 2(2/3)^{\frac{1}{2}}\lambda x + (2\sqrt{2}/3)\lambda y + \tfrac{2}{3}\lambda z + \lambda^2,$$

[16] H. Staudinger and W. Heuer, Ber. **68**, 1618 (1935); Trans. Faraday Soc. **32**, 323 (1936).
[17] K. G. Blaikie and R. N. Crozier, Ind. Eng. Chem. **28**, 1155 (1936).
[18] R. G. W. Norrish and E. F. Brookman, Proc. Roy. Soc. (London) **A163**, 205 (1937).
[19] P. J. Flory, J. Am. Chem. Soc. **63**, 3083 (1941).

where $s^2=x^2+y^2+z^2$. Adding these four equations one obtains

$$\sum_{i=1}^{4} r_i^2=4(s^2+\lambda^2)$$

which is Eq. (11).

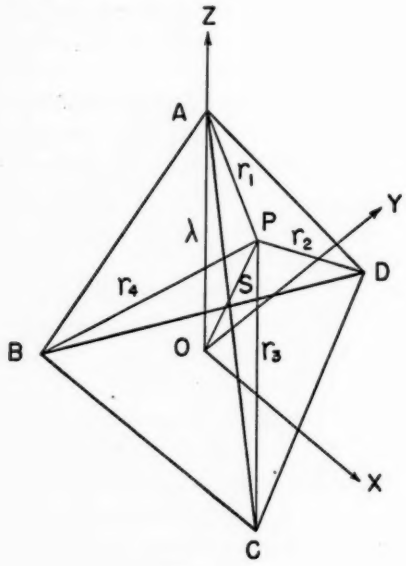

FIG. 3.

Case 2

Let the tetrahedron of Fig. 3 be subjected to a homogeneous lateral compression in such a manner that the resulting irregular pyramid conforms to the following conditions: (1) its y and z dimensions are increased in the ratios γ and α, respectively; (2) the vector AO remains perpendicular to the base; (3) YOZ remains a plane of symmetry; and (4) the volume of the pyramid is unchanged. The geometry of the distorted solid then leads to the following values:

$$r_1^2=s^2-2\alpha\lambda z+\alpha^2\lambda^2,$$
$$r_2^2=s^2-(4\sqrt{2}/3\alpha^{\frac{1}{2}})\gamma\lambda y+(8/9\alpha)\gamma^2\lambda^2+\tfrac{2}{3}\alpha\lambda z+\tfrac{1}{9}\alpha^2\lambda^2,$$
$$r_3^2=s^2-(2(2/3)^{\frac{1}{2}}/\alpha^{\frac{1}{2}}\gamma)\lambda x+(2/3\alpha\gamma^2)\lambda^2+(2\sqrt{2}/3\alpha^{\frac{1}{2}})\gamma\lambda y+(2/9\alpha)\gamma^2\lambda^2+\tfrac{2}{3}\alpha\lambda z+\tfrac{1}{9}\alpha^2\lambda^2,$$
$$r_4^2=s^2+(2(2/3)^{\frac{1}{2}}/\alpha^{\frac{1}{2}}\gamma)\lambda x+(2/3\alpha\gamma^2)\lambda^2+(2\sqrt{2}/3\alpha^{\frac{1}{2}})\gamma\lambda y+(2/9\alpha)\gamma^2\lambda^2+\tfrac{2}{3}\alpha\lambda z+\tfrac{1}{9}\alpha^2\lambda^2.$$

Therefore

$$\sum_{i=1}^{4} r_i^2=4[s^2+\lambda^2(\alpha^2+\gamma^2/\alpha+1/\alpha\gamma^2)/3].$$

If $\gamma=1$, this formula reduces to Eq. (17), while the condition $\gamma=\alpha=1$ gives Eq. (11). It is also seen that the stretch factors can be transposed in the above formula without changing its symmetry, as would be expected on the basis of an assumption of isotropy.

APPENDIX II

According to Eqs. (10) and (11) the probability that the four chain ends terminate in the same volume element $\Delta\tau$ is given by

$$\Omega(\lambda,x,y,z)(\Delta\tau)^4=(\beta^{12}/\pi^6)\exp[-4\beta^2(x^2+y^2+z^2+\lambda^2)](\Delta\tau)^4.$$

By translating the origin in Fig. 3 from the center O of the tetrahedron to the apex A, and changing to spherical coordinates, there is obtained

$$\Omega(\lambda,r,\theta,\varphi)dV=(\beta^{12}/\pi^6)\times\exp[-4\beta^2(r^2+2\lambda r\cos\varphi+2\lambda^2)]r^2\sin\varphi d\varphi d\theta dr,$$

where φ is the angle OAP. Integration over the sphere of radius r gives the probability that the four chain ends lie at the point P at a distance r from A. It is found that

$$\int_{\text{sphere}}\Omega dS=(\beta^{10}/2\pi^5\lambda)\exp[-4\beta^2(r^2+2\lambda^2)]\cdot\sinh(8\beta^2\lambda r)rdr.$$

If this expression is divided by the probability Ω_0 [Eq. (12)] that the four chain ends terminate in the same volume element located any place, the ratio $F(r)$ will give the probability that the volume element containing the chain termini lies in the spherical shell between r and $r+dr$; in other words, $F(r)$ is the probability that a constituent chain has a displacement length r. Therefore

$$F(r)dr=\int_{\text{sphere}}\Omega dS\Big/\Omega_0(\lambda)=(4\beta/\pi^{\frac{1}{2}}\lambda)\exp[-4\beta^2(r^2+\lambda^2)]\cdot\sinh(8\beta^2\lambda r)rdr.$$

Letting $x=r/\lambda$, the above expression gives Eq. (20).

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Statistical Mechanics of Cross-Linked Polymer Networks

II. Swelling

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The interaction of solvents with cross-linked network structures, such as occur in vulcanized rubber, is subjected to a statistical mechanical treatment based on the model and procedure presented in the preceding paper. The activity of the solvent is expressed as a function of its concentration in the swollen network, and of the degree of cross-linking. The maximum degree of swelling of the network in contact with the pure solvent is related to the degree of cross-linking. The heat of interaction of the solvent with the network can be calculated from the temperature coefficient of maximum swelling. The theory leads to the conclusion that the swelling capacity should be diminished by the application of an external stress. Furthermore, the modulus of elasticity should decrease inversely with the cube root of the swelling volume.

IN the field of high polymers there are numerous examples of materials which absorb large quantities of suitable solvents without dissolving. Vulcanized rubber, vinyl-divinyl copolymers, and lightly gelled thermosetting resins when placed in solvents swell through imbibition to a degree depending on the solvent and the structure of the polymer. The original shape is preserved, and the swollen gel exhibits elastic rather than plastic properties.

This phenomenon of limited swelling is characteristic of polymers possessing network structures. If the network structure is permanent in the sense that its essential skeletal structure is not disrupted by the action of the solvent, a state of equilibrium swelling may be attained. As more and more solvent is absorbed (dissolved) by the polymer the network is progressively expanded. The chains connecting multifunctional network junction points are forced to assume more elongated, less probable, configurations. Consequently, a decrease in chain configurational entropy is produced by swelling. Opposing this, an increase in entropy of mixing of solvent with polymer accompanies swelling. Overlooking for the present the effects of the heat of mixing of solvent and polymer, equilibrium will be attained when these opposing entropies, the entropy of chain configuration and the osmotic, or mixing, entropy, become equal in magnitude.

This criterion for swelling equilibrium was recognized by Frenkel,[1] on the basis of which he attempted a rough calculation of the swelling limit for vulcanized rubber. Although he succeeded in introducing an expression for the chain configuration entropy (based on Kuhn's treatment of elasticity) which is appropriate as to order of magnitude, Frenkel concluded that his attempt to use entropies of mixing calculated from ideal solution laws (derived for molecules of equal size) was unsound.

Recently Huggins[2] and one of us[3] derived expressions for the entropy of mixing of small molecules with long chain polymers. Calculated partial molal entropies are in good agreement with those observed by Gee and Treloar[4] for the system benzene-rubber, except at low concentrations of rubber.[5] Using these expressions it is possible to calculate the entropy change due to mixing of solvent molecules with chains of the network structure. The chain configurational entropy change resulting from expansion of the network can be derived from the tetrahedral model discussed in the preceding paper. Com-

[1] J. Frenkel, Acta Physicochimica, U.S.S.R. **9**, 235 (1938); Rubber Chem. Tech. **13**, 264 (1940).

[2] M. L. Huggins, J. Phys. Chem. **46**, 151 (1942); Ann. N. Y. Acad. Sci. **43**, 1 (1942); J. Am. Chem. Soc. **64**, 1712 (1942).

[3] P. J. Flory, J. Chem. Phys. **10**, 51 (1942).

[4] G. Gee and L. R. G. Treloar, Trans. Faraday Soc. **38**, 147 (1942).

[5] While the theory appears to give remarkably good agreement with experiment at high polymer concentrations, we agree with Gee and Treloar that some improvement at low concentrations is desirable. The theory is notably unsatisfactory in very dilute solutions; see, P. J. Flory, J. Am. Chem. Soc. **65**, 372 (1943). These matters have been discussed in detail elsewhere (paper presented before the Division of Physical and Inorganic Chemistry at the Pittsburgh Meeting of the American Chemical Society, Sept. 6, 1943).

bining these, there is obtained the total entropy of mixing of solvent with cross-linked polymer, from which activities of solvent and the swelling limit can be computed, as well as their dependence on the structure of the network.

THE ENTROPY OF SWELLING

Paralleling the procedure followed in the preceding paper (I), the formation of a network composed of ν chains bound together by $\nu/2$ cross-linkages will be considered to involve a cycle composed of the following steps:

(*D*) Dilution of ν chains (prior to cross-linking) with n solvent molecules.

(*A*) Cross-linking of groups of four chains, as in I (*A*) except as modified by the presence of diluent.

(*B*) Conversion of these groups to the final network through the introduction of $\nu/4$ cross-linkages, as in I (*B*) except as modified by diluent.

(*C*) Linear combination of the *undiluted* chains to form very long polymer molecules, exactly as in I (*C*).

In addition to the assumption employed in the preceding paper, we assume here that the configurations of the ν chains are essentially unaltered by the dilution process, the distribution of chain displacement lengths being given by I (2) both before and after dilution. Furthermore, we assume the validity of the entropy of mixing expression, previously referred to,[2,3] as applied to step (*D*); i.e.,

$$\Delta S_D = -k\left[n \ln\left(\frac{n}{n+Z\nu}\right)+\nu \ln\left(\frac{Z\nu}{n+Z\nu}\right)\right], \quad (1)$$

where Z is the number of segments per chain, the size of the segment being taken equal in volume to one solvent molecule.[6]

Processes (*A*) and (*B*) differ from the corresponding steps of the preceding paper only insofar as they are affected by the greater volume of the system containing solvent molecules. In the swollen network the points of cross-linkage are distributed over a larger volume. Hence, the tetrahedral cells will be proportionately enlarged. The dimension λ' of the average tetrahedral cell (assumed to be a regular tetrahedron) in the swollen state is related to λ for the unswollen network according to

$$\lambda'/\lambda = (V'/V)^{\frac{1}{3}} = 1/v_2^{\frac{1}{3}}, \quad (2)$$

where V and V' are the volumes of the polymer and of the swollen network, respectively, and v_2 is the volume fraction of polymer in the swollen gel.

The entropy change for the process

Long polymer molecules→swollen network

will be given by

$$\Delta S_v' = \Delta S_D + \Delta S_A + \Delta S_B - \Delta S_C. \quad (3)$$

ΔS_A is given by Eq. I (9) wherein V is replaced by V', and ΔS_B is given by Eq. I (13) with λ replaced by λ'. Inasmuch as step (*C*) takes place in the absence of diluent, ΔS_C is given by I (14). Replacing $Z\nu/(n+Z\nu)$ in (1) with V/V' and substituting the various expressions in (3),

$$\begin{aligned}\Delta S_v' = k\nu\{&-(n/\nu)\ln[n/(n+Z\nu)]\\ &+\tfrac{3}{4}\ln(\beta^3/\pi^{\frac{3}{2}})-\beta^2\lambda'^2\\ &+\tfrac{3}{2}\ln\Delta\tau+\tfrac{1}{4}\ln\Delta\tau'-\ln\Delta\tau''-\ln 2\}. \quad (4)\end{aligned}$$

Subtracting I (15) from (4), there is obtained for the entropy of swelling

$$\begin{aligned}\Delta S_s = \Delta S_v' - \Delta S_v &= -kn\ln[n/(n+Z\nu)]\\ &\quad -k\nu\beta^2(\lambda'^2-\lambda^2). \quad (5)\end{aligned}$$

If the actual cross-linking process occurs in the unswollen state under conditions of random coiling and entanglement of the chains, then we may identify λ with an average chain displacement length. Letting

$$\lambda^2 = \overline{r^2} = 3/2\beta^2$$

and substituting for $(\lambda'/\lambda)^2$ from Eq. (2),

$$\begin{aligned}\Delta S_s &= -kn\ln[n/(n+Z\nu)]\\ &\quad -(3/2)k\nu[(V'/V)^{\frac{2}{3}}-1]\\ &= -kn\ln[n/(n+Z\nu)]\\ &\quad -(3/2)k\nu\left[\left(\frac{n+Z\nu}{Z\nu}\right)^{\frac{2}{3}}-1\right]. \quad (6)\end{aligned}$$

The first term in (6) represents the entropy of mixing of polymer and solvent; the second term represents the "elastic" entropy change arising

[6] This arbitrary definition of the segment size is of no consequence in the final results.

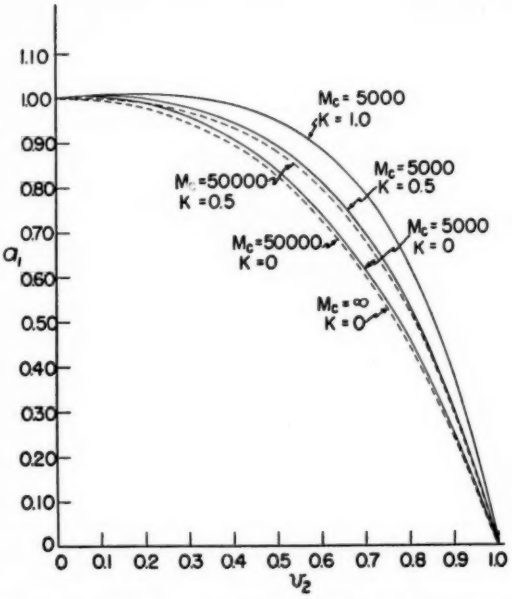

FIG. 1. Activities of solvent dissolved in cross-linked polymer as a function of volume fraction of polymer v_2, for several values of the molecular weight M_c of the chain between cross-linkages and of the heat of mixing constant K.

from deformation of the network. The latter term is approximately three times the entropy of deformation given by Eq. I (19′) for small deformations, if we identify $(V'/V)^{\frac{1}{3}}$ with α.

Differentiating (6) with respect to n and substituting $v_2=Zv/(n+Zv)$, there is obtained for the partial molal entropy of dilution

$$\Delta\bar{S}_1=-R[\ln(1-v_2)+v_2]-(R/Z)v_2^{\frac{1}{3}}$$
$$=-R[\ln(1-v_2)+v_2]-(R\rho V_1/M_c)v_2^{\frac{1}{3}}, \quad (7)$$

where V_1 is the molar volume of the solvent, ρ is the density of the polymer, and M_c is the molecular weight of the chain.

If we assume a van Laar heat of dilution term given by

$$\Delta\bar{H}_1=BV_1v_2^2,$$

where B is a constant depending on the components, polymer and solvent, then the partial molal free energy becomes

$$\Delta\bar{F}_1=RT[Kv_2^2/2+\ln(1-v_2)+v_2+(\rho V_1/M_c)v_2^{\frac{1}{3}}], \quad (8)$$

where $K=2BV_1/RT$. Or, upon expanding the logarithmic term

$$\Delta\bar{F}_1=RTv_2^2[(K-1)/2-v_2/3-v_2^2/4-\cdots]+(RT\rho V_1/M_c)v_2^{\frac{1}{3}}. \quad (8')$$

When the equation corresponding to (8) for the partial molal free energy of dilution of soluble (not cross-linked) polymers is compared with experimental thermodynamic data for dilute polymer solutions, K is found to include terms other than the heat of mixing term.[2,5] Thus, K appears to be separable into two parts:

$$K=A+2BV_1/RT, \quad (9)$$

where A is an empirical parameter the origin of which is not yet clear. Whether or not such a term should be included for cross-linked systems is not known. Here we shall bear in mind that K may include such a term, and in particular, that K should not necessarily be assigned the value zero when the heat of mixing is negligible.

ACTIVITY OF SOLVENT

In Fig. 1 activities a_1 calculated from Eq. (8) and the relationship

$$\ln a_1=\Delta\bar{F}_1/RT$$

are plotted against v_2 for several values of M_c and K. The same curves are shown in Fig. 2 on an enlarged scale covering the low concentration region. The $M_c=\infty$ curve represents a mixture of solvent with infinitely long polymer molecules in the absence of cross-linkages. There is neither a maximum nor a minimum, the curve becoming tangentially horizontal at $v_2=0$. The curve (not shown) for linear molecules of finite length approaches $a_1=1$ at $v_2=0$ with a finite *negative* slope which is inversely proportional to the molecular weight. With the addition of cross-linkages and conversion of the polymer to a network structure the activity-concentration curve assumes a *positive* slope at $v_2=0$, the magnitude of the slope being inversely proportional to M_c, i.e., directly proportional to the "concentration" of cross-linkages in the network. Thus, it is possible to trace the progressive changes in the thermodynamics of the system polymer: solvent proceeding from relatively small linear polymers to infinitely long molecules to cross-linked networks of increasing degrees of cross-linking.

The appearance of a maximum in an activity-composition diagram requires that the components exhibit partial miscibility. We may conclude on strictly thermodynamical grounds that

complete miscibility is no longer possible when M_c is finite (i.e., with the appearance of a network structure) since the a_1 *vs.* v_2 curves then possess maxima. The activities for the two phases in equilibrium must be the same. Furthermore, compositions in which the activity of the solvent is greater than that of the pure solvent are necessarily inaccessable. Hence, one of the phases must be pure solvent, and the other will have the composition corresponding to the intersection of the curve with the $a_1=1$ ordinate.

These characteristics of the solvent-network system are evident from considerations of the limitations on the polymer imposed by its network structure. It is of interest, nevertheless, to point out that they can be derived by the formal statistical-thermodynamical procedure outlined above. From a quantitative point of view, this procedure predicts the composition of the swollen phase in equilibrium with pure solvent (*cf. seq.*).

When K is not zero, due to a heat of mixing or for other reasons as mentioned above the curves are shifted as shown in Figs. 1 and 2 for $K=0.5$ and $K=1$; these values correspond to moderately unfavorable (endothermic) heats of interaction of the components. The general character of the curve is not changed. For all values of K the curves retain their single maxima. The greater the value of K (algebraically) the higher the curve, the greatest effect on a_1 being shown at high concentrations of polymer. Maximum swelling, corresponding to $a_1=1$, is less the greater the value of K.

The effects of the cross-linkages on the system are by no means restricted to the region of maximum swelling, as Gee[7] has assumed in his semi-empirical analysis of the interaction of solvents with vulcanized rubber. The effect of a moderate degree of cross-linking on the magnitude of the activity is small, but it persists to the highest concentration of polymer; in fact, the percentage increase in a_1 due to the cross-linkages increases somewhat with increase in v_2. This is evident from the form of Eq. (8). It can be shown that the Henry's law constant becomes

$$(da_1/dv_1)_{v_2=0}=\exp\left[(1+K/2)+\rho V_1/M_c\right], \quad (10)$$

[7] G. Gee, Trans. Faraday Soc. **38**, 418 (1942).

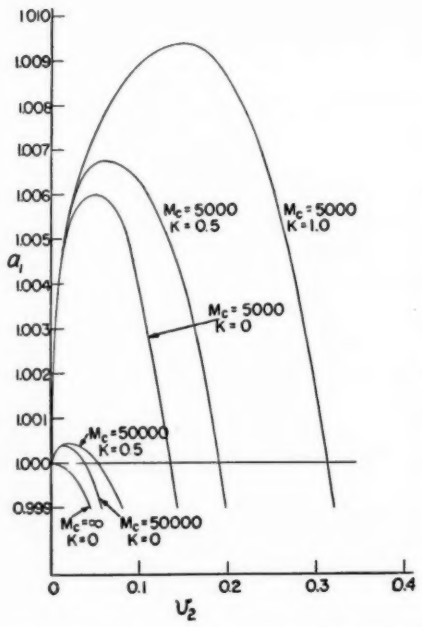

FIG. 2. Activity—composition diagram in the region of high solvent concentration.

the second term in the exponent representing the increase in the activity of the solvent due to the reaction of the network structure. This term is very small, except for high degrees of cross-linking (low M_c).

SWELLING EQUILIBRIUM

At equilibrium with pure solvent $\Delta\bar{F}_1=0$. Equating Eq. (8) to zero,

$$M_c=-\rho V_1 v_2^{\frac{1}{3}}/[Kv_2^2/2+\ln(1-v_2)+v_2], \quad (11)$$

where v_2 represents the volume fraction of polymer in the swollen gel which is in equilibrium with pure solvent. Alternatively, v_2 is the reciprocal of the "swelling volume," the latter being defined as the ratio of the swollen volume (at equilibrium) to the initial volume. If the degree of swelling is large (v_2 small) higher terms in the series expansion of $\ln(1-v_2)$ may be dropped, giving

$$M_c \backeq 2\rho V_1/v_2^{5/3}(1-K). \quad (12)$$

Or,

$$v_2 \backeq [2\rho V_1/M_c(1-K)]^{3/5}. \quad (13)$$

Thus the reciprocal swelling volume in a given solvent is approximately inversely proportional to the three-fifths power of the average molecular

weight per chain, or directly proportional to the three-fifths power of the concentration of cross-linkages, provided of course, the degree of swelling is large. For lower degrees of equilibrium swelling v_2 can be computed from Eq. (10), which is not explicitly solvable for v_2.

Generally M_c is not known, but v_2 is readily measurable by any one of several methods.[8] These relationships provide a means for estimating the degree of cross-linking, or M_c, from the swelling volume. The absolute significance of the values so obtained will be limited by the uncertainty in the value of K and by some of the approximations employed in the derivation of the basic Eq. (6). However, relative values so obtained should be of considerable utility in characterizing the structure of cross-linked networks.

TEMPERATURE COEFFICIENT OF SWELLING

Continuing under the assumption that the heat of mixing can be represented by a van Laar term, the temperature coefficient of maximum swelling can be calculated from the stipulation that $\Delta\bar{F}_1=0$ at all temperatures. Then

$$(dv_2/dT)_{a_1=1}=-(\partial\Delta\bar{F}_1/\partial T)_{v_2}/(\partial\Delta\bar{F}_1/\partial v_2)_T. \quad (14)$$

Assuming that $A=0$ in Eq. (9), then on differentiating Eq. (8) with respect to temperature and employing the above condition there is obtained

$$(\partial\Delta\bar{F}_1/\partial T)_{v_2}=-RKv_2^2/2.$$

Similarly,

$$\begin{aligned}(\partial\Delta\bar{F}_1/\partial v_2)_T&=RT[Kv_2-v_2/(1-v_2)\\&\qquad+\rho V_1/(3M_cv_2^{\frac{1}{3}})]\\&=RT\{5Kv_2/6-v_2/(1-v_2)\\&\qquad-(1/3)[1+\ln(1-v_2)/v_2]\}.\end{aligned}$$

Substituting these expressions in (14) and expanding the denominator in series,

$$dv_2/dT=Kv_2/2T\left[\frac{5}{6}-(K-1)-\frac{8}{9}v_2-\frac{11}{12}v_2^2-\frac{14}{15}v_2^3-\cdots\right]. \quad (15)$$

Or

$$d\ln v_2/d\ln T=K/2\left[\frac{5}{6}-(K-1)-\frac{8}{9}v_2-\frac{11}{12}v_2^2-\cdots\right]. \quad (15')$$

Thus from the change of the swelling volume $(1/v_2)$ with temperature values of K, or of the heat of mixing constant B, can be computed. For very small values of K and high degrees of swelling (small v_2)

$$d\ln v_2/d\ln T\cong -3K(1-v_2)/5(1-K). \quad (15'')$$

EFFECT OF DEFORMATION ON SWELLING

In analogy with Eq. I (18) for the entropy of formation of an elastically deformed network, there is obtained for the entropy change in the process

Long polymer molecules $\rightarrow$ swollen, elongated network

$$\begin{aligned}\Delta S_v''=k\nu\{&-(n/\nu)\ln[n/(n+Z\nu)]\\&+(3/4)\ln(\beta^3/\pi^{\frac{1}{2}})\\&-\beta^2\lambda'^2(\alpha^2+2/\alpha)/3+\text{const.}\},\end{aligned} \quad (16)$$

where α is the ratio of the length of the elongated, swollen specimen to its length in the unstressed, swollen condition. For the entropy change in passing from the unstressed unswollen condition to the elongated, swollen state

$$\Delta S_{d,s}=-kn\ln[n/(n+Z\nu)]-k\nu\beta^2\lambda^2\left[\left(\frac{n+Z\nu}{Z\nu}\right)^{\frac{1}{3}}\left(\alpha^2+\frac{2}{\alpha}\right)\Big/3-1\right]. \quad (17)$$

Differentiating (17) with respect to n, and letting $\beta^2\lambda^2=\frac{3}{2}$, the partial molal free energy of the solvent becomes

$$\begin{aligned}\Delta\bar{F}_1=RT[&Kv_2^2/2+\ln(1-v_2)+v_2\\&+(\rho V_1/M_c)(\alpha^2+2/\alpha)v_2^{\frac{1}{3}}/3].\end{aligned} \quad (18)$$

Thus, the activity of the solvent is increased by deformation of the gel. A gel which is in equilibrium with pure solvent should de-swell on stretching. Upon equating (18) to zero, there is obtained for the approximate volume fraction of polymer in the elongated gel at equilibrium with pure solvent

$$v_2\cong[2\rho V_1(\alpha^2+2/\alpha)/3M_c(1-K)]^{3/5} \quad (19)$$

[8] C. M. Blow and P. Stamberger, Recueil Travaux Chimique Pays Bas **48**, 64 (1929); J. R. Scott, Trans. Inst. Rubber Ind. **5**, 95 (1929); I. Williams, Ind. Eng. Chem. **29**, 172 (1937); G. S. Whitby, A. B. A. Evans, and D. S. Pasternack, Trans. Faraday Soc. **38**, 269 (1942).

which differs from Eq. (13) by the factor $[(\alpha^2+2/\alpha)/3]^{3/5}$. The swollen volume of the gel at equilibrium should decrease by this factor upon elongating the gel to a length α times its initial length.

EFFECT OF SWELLING ON ELASTIC PROPERTIES

Differentiation of Eq. (17) with respect to the length $L=\alpha L_0'$ of the swollen specimen gives the retractive force

$$f'=(\partial\Delta F/\partial L)=-T(\partial\Delta S/\partial L)$$
$$=(RT\nu/L_0'v_2^{\frac{1}{3}})(\alpha-1/\alpha^2),$$

where L_0' is the initial length of the unstretched, swollen gel. Since

$$\nu/L_0'=\rho v_2 A_0'/M_c,$$

where A_0' is the cross-sectional area of the unstretched, swollen gel,

$$f'=(RT\rho A_0'v_2^{\frac{1}{3}}/M_c)(\alpha-1/\alpha^2). \qquad (20)$$

The modulus of elasticity of the gel, referred to its initial cross-sectional area in the swollen condition, becomes

$$\epsilon'=(RT\rho v_2^{\frac{1}{3}}/M_c)(1+2/\alpha^3) \qquad (21)$$

which differs from Eq. I (6) for unswollen polymer by the factor $v_2^{\frac{1}{3}}$. Thus, the modulus of elasticity of the gel should decrease with the inverse cube root of the volume degree of swelling $1/v_2$.

If stresses are to be calculated on the basis of the initial cross section A_0 before swelling, then

$$f=(RT\rho A_0/v_2^{\frac{1}{3}}M_c)(\alpha-1/\alpha^2) \qquad (22)$$

and

$$\epsilon=(RT\rho/v_2^{\frac{1}{3}}M_c)(1+2/\alpha^3), \qquad (23)$$

where α is retained as the strain referred to the unstretched, swollen length. Hence, the retractive force at a given strain factor α should increase with swelling in proportion to $1/v_2^{\frac{1}{3}}$.

EFFECTS OF DILUENTS INTRODUCED PRIOR TO CROSS-LINKING (OR VULCANIZATION)

Throughout the above discussion it has been assumed that cross-linking occurs in the absence of inert diluents and that all of the polymer becomes bound into the network. If diluent, or other material which is not incorporated into the network, is present when cross-linking occurs, the basic network structure will differ from that formed in the absence of diluent. If the same number $\nu/2$ of chemical cross-bonds are presumed to be introduced in the presence of diluent obviously they will be separated by greater average distances in the network. Since we assume that the configurations of the individual molecules are unaltered by dilution, the contour length of the chain, and M_c, will be increased by dilution prior to cross-linking. But this conclusion is inconsistent with the obvious requirement that

$$\nu M_c=\text{constant}. \qquad (24)$$

This apparent paradox arises from our failure to consider intramolecular cross-linkages which

unite two points of the same linear molecule. They contribute nothing to the network structure. An approximate statistical calculation shows that the relative number of such bonds will be comparatively small in the absence of diluent, but that it will increase rapidly with dilution. In Eq. (24) we should use a ν value corrected for the proportion of these intra-chain linkages. This corrected ν will decrease as M_c is increased by dilution. Qualitatively, at least, this is consistent with (24).

The physical properties of a network formed in the presence of diluent will differ from those of a network formed in absence of diluent and subsequently swollen. For the same total number of cross-bonds there will be fewer significant cross-bonds in the former. Furthermore, the quantity $\beta^2\lambda^2$ which enters into the above calculations will be less, thus lowering the elastic moduli, and increasing the swelling capacity.

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Statistical Thermodynamics of Rubber. III[1]

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A basic postulate used by Treloar and by the author in recent theories of rubber elasticity is reexamined and its equivalent is derived from more fundamental considerations. The postulate dealt with the distribution of molecular lengths in a sample of strained rubber. Equations of state for rubber-like materials are derived by using the conventional methods of statistical mechanics. The results are found to be equivalent to those obtained by other means.

THE kinetic theories of rubber elasticity which have been developed within recent years[1,2] have grown out of one fundamental idea, namely that the elastic forces involved are due to the thermal motions of the molecules rather than to deformations of valence bonds and angles. In deriving theoretical equations of state for rubber, the usual procedure has been to connect entropy concepts with the probability functions for molecular shapes, assuming that molecules can have different shapes as a result of rotation about some of the valence bonds. Although the various authors[1,2] started with substantially the same idea their theories differed as to the way in which entropy changes were calculated. Recently, however, Treloar[3] has shown that by eliminating certain approximations from Kuhn's treatment,[2e] then Kuhn's theory gives precisely the same result as does the theory of the present author.[1]

A basic postulate of the author's theory and of Kuhn's theory as amended by Treloar is that when a piece of rubber is deformed, the components of the lengths of the molecules will change in the same ratio as the corresponding dimensions of the rubber. To illustrate this specifically, let us consider a one-dimensional problem. If x is the component of the length of a molecule in the direction under consideration, then for a piece of unstrained rubber the probability of finding a molecule with a value of x in the range x to $x+dx$ will be given by

$$p(x)dx=(\beta/\pi^{\frac{1}{2}})\exp(-\beta^2x^2)dx \qquad (1)$$

where β is a parameter depending upon the nature of the molecular chains. According to the above-mentioned postulate, when the rubber is stretched by a factor α, then the distribution function becomes

$$p'(x)dx=(\beta/\pi^{\frac{1}{2}}\alpha)\exp(-\beta^2x^2/\alpha^2)dx. \qquad (2)$$

Although Eq. (2) is highly plausible and provides a convenient start for a theory of elasticity, it would be well to look into the reasons underlying it. One of the purposes of the present paper is to derive Eq. (2) from more fundamental considerations. This will be accomplished by showing that (2) is the most probable distribution compatible with the strained condition of the rubber, it being assumed that (1) represents the distribution for the unstrained material.

A rubber network presumably consists of molecules linked together at various places by means of vulcanization bridges. Starting at one end of a piece of bulk rubber one should be able to reach the other end by following a more or less random path of molecules through the network (Fig. 1). Going from one end to the other by a random path involves a large number of molecules and the path will include numerous retrogressions from as well as advancements toward the ultimate goal. It should be recognized that a few conceivable paths might involve a relatively small number of molecules if the paths happen to be fairly straight. Other paths on the other hand can involve an unduly large number of molecules. We shall here consider a typical random path involving, let us say, n molecules.

[1] For the first two papers of this series see (a) F. T. Wall, J. Chem. Phys. **10**, 132 (1942); (b) F. T. Wall, J. Chem. Phys. **10**, 485 (1942).
[2] (a) K. H. Meyer, G. von Susich and E. Valko, Kolloid Zeits. **59**, 208 (1932). (b) E. Guth and H. Mark, Monats. Chem. **65**, 93 (1934). (c) W. Kuhn, Kolloid Zeits. **68**, 2 (1934); **76**, 258 (1936). (d) E. Guth and H. M. James, Ind. Eng. Chem. **33**, 624 (1941); **34**, 1365 (1942).
[3] L. R. G. Treloar, Trans. Faraday Soc. **34**, 36 (1943).

If l equals the over-all length of the rubber, then

$$l=x_1+x_2+x_3+\cdots x_n \tag{3}$$

where the x's denote the components of the lengths of the molecules in the direction considered. It should be noted that the x's can have positive or negative values and that l is measured by their algebraic sum and not by the sum of their absolute values. Squaring (3) there is obtained

$$\begin{aligned} l^2=&x_1^2+x_2^2+x_3^2+\cdots x_n^2 \\ &+2(x_1x_2+x_2x_3+\cdots x_{n-1}x_n) \\ &+2(x_1x_3+x_2x_4+\cdots x_{n-2}x_n)+\cdots. \end{aligned} \tag{4}$$

Since n is large we can simplify (4) by introducing averages, thus obtaining

$$\begin{aligned} l^2=&n\langle x^2\rangle_{Av}+2(n-1)\langle x_ix_{i+1}\rangle_{Av} \\ &+2(n-2)\langle x_ix_{i+2}\rangle_{Av}+\cdots. \end{aligned} \tag{5}$$

But because n is large and the path is random all of the averages appearing in (5) except $\langle x^2\rangle_{Av}$ will approach zero since the x's are divided almost equally between positive and negative values. Making use of this fact it is seen that

$$l^2=n\langle x^2\rangle_{Av}. \tag{6}$$

Equation (6) is not exact but is an excellent approximation for the purpose in mind. As a matter of fact, Eq. (6) will give exactly the mean square length of a large number of chains of n members, the average square lengths of the members being $\langle x^2\rangle_{Av}$, providing the chains are not subject to any boundary constraints. Since for the problem at hand the chains must begin and end in certain planes and cannot have any portions outside the boundaries of the bulk rubber, some degree of randomness is lost thereby rendering (6) an approximation.

From Eq. (6) we conclude that the over-all length of a piece of rubber is proportional to the root mean square length of the molecules, referring of course to components in the specified direction. Accordingly if a piece of rubber is stretched from a length l to αl, then the root mean square length of the molecules must be increased by a factor α. This statement is considerably more general than saying that *each* molecule has its length component changed by a factor α, for there are obviously many other ways of changing the root mean square length by a given factor.

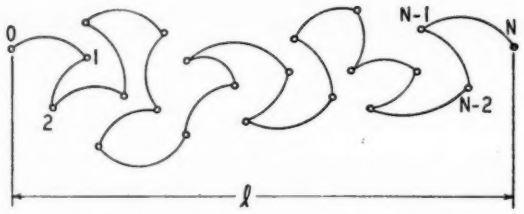

FIG. 1. Random molecular path involving n molecules passing through network of rubber of length l. Small circles denote vulcanization bridges each of which probably link together four "molecules." (To avoid confusion no side links are shown in the figure.)

There will now be derived the most probable distribution of molecular lengths consistent with a given macroscopic length for the piece of rubber. For convenience the one-dimensional problem will be considered first and the extension to three dimensions made later.

Let us divide the x space of the molecules into a number of cells of size Δx_i, each cell being located in the neighborhood of x_i. Let the probability that a molecule have an x value in the range of Δx_i be p_i. Then from (1) we have

$$p_i=(\beta/\pi^{\frac{1}{2}})\exp(-\beta^2x_i^2)\Delta x_i. \tag{7}$$

Let N_i equal the number of molecules with x values in the range Δx_i and N equal the total number of molecules. Then the number of permutations associated with the statistical state specified by N_0, N_1, N_2, $\cdots$, etc. will be given by

$$W=\frac{N!}{N_0!N_1!N_2!\cdots}p_0^{N_0}p_1^{N_1}p_2^{N_2}\cdots. \tag{8}$$

Two conditions of constraint can be applied to Eq. (8), namely:

$$N=\sum_i N_i \tag{9}$$

and

$$l^2=C\sum_i N_ix_i^2. \tag{10}$$

Condition (9) simply requires the correct sum for the total number of molecules and condition (10), in which C is a constant, is equivalent to (6).

The statistical problem can now be carried

out in the usual way.[4] To find the most probable distribution we make use of Stirling's approximation and note that

$$\delta \ln W=\sum_i (-\ln N_i+\ln p_i)\delta N_i=0,$$
$$\delta N=\sum_i \delta N_i=0 \tag{11}$$

and

$$\delta l^2=C\sum_i x_i^2\delta N_i=0.$$

Introducing Lagrangian multipliers in the conventional manner and solving for N_i there is obtained

$$N_i=p_i \exp(\lambda+\mu x_i^2) \tag{12}$$

where the multiplier μ has absorbed the constant C. Putting in the value for p_i it is seen that

$$N_i=(\beta/\pi^{\frac{1}{2}}) \exp\{\lambda-(\beta^2-\mu)x_i^2\}\Delta x_i \tag{13}$$

or in a differential form

$$dN=(\beta/\pi^{\frac{1}{2}}) \exp\{\lambda-(\beta^2-\mu)x^2\}dx. \tag{14}$$

From (14) it follows that

$$N=\frac{\beta e^\lambda}{\pi^{\frac{1}{2}}}\int_{-\infty}^{\infty} \exp\{-(\beta^2-\mu)x^2\}dx=\frac{\beta e^\lambda}{(\beta^2-\mu)^{\frac{1}{2}}}. \tag{15}$$

Eliminating e^λ from (14) and (15) we see that

$$dN=\frac{N(\beta^2-\mu)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \exp\{-(\beta^2-\mu)x^2\}dx. \tag{16}$$

But from (10) and (16) it follows that

$$l^2=\frac{CN(\beta^2-\mu)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}}$$
$$\times\int_{-\infty}^{\infty} x^2 \exp\{-(\beta^2-\mu)x^2\}dx=\frac{CN}{2(\beta^2-\mu)}. \tag{17}$$

It is clear from (16) that the piece of rubber must be in its natural unstrained state when $\mu=0$, under which condition $l=l_0$. Hence from (17),

$$l_0^2=CN/2\beta^2 \tag{18}$$

from which it follows that

$$\alpha^2=(l/l_0)^2=\beta^2/(\beta^2-\mu). \tag{19}$$

[4] See for example Tolman, *Statistical Mechanics* (Oxford University Press, 1938), p. 79, or Mayer and Mayer, *Statistical Mechanics* (John Wiley, 1940), p. 113.

Combining (19) with (16) there is obtained the equivalent of (2), namely:

$$dN=(N\beta/\pi^{\frac{1}{2}}\alpha) \exp(-\beta^2x^2/\alpha^2)dx. \tag{20}$$

The foregoing treatment shows that (2) or (20) must be the most probable distribution compatible with an increase in root mean square length by a factor α. Although (2) was a very plausible postulate, the present treatment strengthens it by showing what ideas are implicit in it. For one thing it is not necessary to suppose that each molecule is extended in the same way as the mass of rubber. Thus the postulatory basis of the theory of rubber elasticity has been pushed back at least one step toward more fundamental concepts such as are illustrated in Fig. 1 and expressed by Eqs. (3) to (6).

It is important that one deal with the root mean square length rather than with the average of the absolute values of the molecular lengths. If condition (10) were replaced by

$$l=C\sum_i |x_i| N_i \tag{21}$$

then Eq. (20) would not be obtained. Instead one would arrive at a less neat distribution function which would ultimately lead to an unwieldy equation of state for rubber. Conditions of type (21) would also make the three-dimensional problem intractable with respect to change of coordinates because the total length of a molecule cannot be taken as the sum of the three components whereas the square of the total length is equal to the sum of the squares of the components. It should not be supposed, however, that (10) is more correct than (21) simply because it is easier to handle, for the theoretical considerations outlined earlier show that (10) is to be expected.

THE EQUATION OF STATE FOR RUBBER

From Eq. (20) it is possible to deduce an equation of state for rubber by using the methods of the author[1] or of Kuhn as amended by Treloar.[3] However another derivation will now be given which parallels the conventional statistical methods. Making use of Boltzmann's relation, the entropy will be given by the expression

$$S=k \ln W_{\max}. \tag{22}$$

Putting in the expression for W and making use of Stirling's approximation, we obtain from (22)

$$S=Nk \ln N-k \sum_i N_i \ln (N_i/p_i). \quad (23)$$

Taking cognizance of (9), (10), and (12) it is found that

$$S=Nk \ln N-Nk\lambda-k\mu l^2/C. \quad (24)$$

Eliminating λ, C, and μ from (24) by use of Eqs. (15), (18), and (19), it is found that

$$S=Nk \ln \alpha-Nk(\alpha^2-1)/2. \quad (25)$$

Equation (25) gives that portion of the entropy which can be associated with deformation effects and is not to be regarded as the total entropy of the rubber. But just as it is possible to deduce a correct equation of state for an ideal gas by considering volume effects alone, so too an equation of state for rubber can be derived by investigating the relationship between entropy and length. Differentiating (25) with respect to length there is obtained

$$dS=-(Nk/l_0)(\alpha-1/\alpha)dl. \quad (26)$$

From the fundamental thermodynamic relation

$$f=-T(\partial S/\partial l)_E \quad (27)$$

where f is the force applied, it follows that

$$f=(NkT/l_0)(\alpha-1/\alpha). \quad (28)$$

Equation (28) is not complete, of course, because only one dimension was considered. However it is precisely the same equation as was derived by the author's earlier method applied to the one-dimensional problem.[1a] Hence the equivalence of the two methods of attack has been demonstrated.

The extension to three dimensions can be carried out immediately. The entropy of the deformed rubber will be given by the sum of expressions of type (25) using α_x, α_y and α_z as the relative stretchings in the x, y and z directions. Thus we see that

$$S=Nk \ln (\alpha_x\alpha_y\alpha_z) -Nk(\alpha_x^2+\alpha_y^2+\alpha_z^2-3)/2. \quad (29)$$

Assuming that rubber is incompressible, it follows that $\alpha_x\alpha_y\alpha_z=1$ which introduces some simplification in (29). If a force is applied in one direction only (say the x direction), then $\alpha_y=\alpha_z=1/(\alpha_x)^{\frac{1}{2}}$ from which it is seen that

$$S=-Nk(\alpha^2+2/\alpha-3)/2 \quad (30)$$

where the subscript x has been dropped from α. From (30) the stretching force is readily calculated to be

$$f=(NkT/l_0)(\alpha-1/\alpha^2) \quad (31)$$

which result is the same as has been derived earlier.[1b,3] The function (31) is also similar to an equation derived by Guth and James.[2d]

By using the methods indicated above it is also possible to show that rubber should obey Hooke's law with respect to shear. A simple shear of amount γ is obtained[5] by taking $\gamma=\alpha-1/\alpha$ where $\alpha=\alpha_x=1/\alpha_y$ and $\alpha_z=1$. From (29) the entropy of shear is calculated to be

$$S=-Nk\gamma^2/2. \quad (32)$$

Hence the shearing moment (L) will be given by

$$L=-T(\partial S/\partial\gamma)_E=NkT\gamma. \quad (33)$$

From (33) it is seen that L is proportional to γ; in other words, Hooke's law is obeyed.

Equations (31) and (33) can be regarded as ideal equations of state for rubber-like substances. This view is justified because of the high degree of correspondence between the derivation and the limitations of Eqs. (31) and (33) and those of the ideal gas law. Actual samples of rubber will not obey the above-mentioned equations exactly for two principal reasons. First the distribution functions (1) and (2) are not valid for large values of x and second the van der Waals interactions have been neglected in the calculations. The errors introduced thereby will increase with increasing deformation. Even if exact distribution functions were used in place of (1) and (2), the equations of state so derived would not be correct for large deformations because of intermolecular attractions and repulsions.

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[5] A. E. H. Love, *Mathematical Theory of Elasticity*, (Cambridge University Press), second edition, p. 34.

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

Statistical Treatment of Imperfectly Flexible Chains

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September 21, 1943

IN our theory of the structure of rubber[1] we have reduced the problem of computing the stress-strain relation for bulk rubber to that of determining the effective stress-extension relation for a single flexible molecular chain with ends separated by a distance comparable to its total length. For qualitative and even semi-quantitative development of the theory it was sufficient to represent the molecular chain by a model consisting of independent links of fixed length taking on all orientations in space with equal statistical weight. For the quantitative development of the theory it is desirable to use a model of the molecular chain giving a better approximation to reality. Perhaps the simplest such model is a chain of links of fixed length, each making a fixed valence angle with its neighbors and permitting free relative rotation of the two parts of the molecule about its axis.

In the present letter we wish to indicate the mathematical methods we have employed in the statistical treatment of this type of flexible chain under thermal agitation. The methods will be discussed in detail and the results employed in comparisons with experiment in a paper now in preparation.

A chain such that the statistical weight for a given extension and orientation of each link depends on the configuration of neighboring links we shall term an imperfectly flexible chain. A large class of these chains, which includes the model we wish to treat, is characterized by the existence of a "joint function" $c(x_1, x_2)$ such that

$$dC = c(x_1, x_2)dx_2 \tag{1}$$

is the relative number of configurations for which the second of two links forming a joint has the x component of its extension equal to x_2 to within dx_2, the adjacent link l having x component x_1. The generating function[1] $G_N(x_1, x_{N+1}; w)$ for a chain of N joints, with the end links constrained to have x components x_1 and x_{N+1}, can be expressed in terms of the joint function. In particular

$$G_N(x_1, x_{N+1}; w) = \int dx_N G_{N-1}(x_1, x_N; w)c(x_N, x_{N+1})w^{(x_N^2+x_{N+1}^2)/2}. \tag{2}$$

The average extension of such a chain under the constant force $Z=fkT$ is then

$$\bar{L}_N(x_1, x_{N+1}) = d[\log G_N(x_1, x_{N+1}; e^f)]/df. \tag{3}$$

Now we may consider the extension of a very long chain under constant force as the sum of three parts:

(1) A part proportional to the number of joints N times the average contribution to the extension of an internal link far from the ends.

(2) An end effect depending on the orientation of end link l, independent of the number of links in the long chain.

(3) A similar end effect depending on the orientation of the other end link.

The corresponding hypothesis concerning the generating function is

$$\lim_{N\to\infty} G_N(x_1, x_{N+1}; w) = q^N(w)r(x_1, w)r(x_{N+1}, w). \tag{4}$$

Introducing this assumption into Eq. (2) we obtain the basic integral equation of this theory,

$$q(w)r(x, w) = \int dy c(x, y)w^{(x^2+y^2)/2}r(y, w). \tag{5}$$

This is a linear homogeneous integral equation which may be of the Fredholm type (limits constant) or Volterra type (limits variable), according to the form of $c(x, y)$. Such integral equations have well-behaved solutions, for a given w, only for discrete values of q, $q_1(w)$, $q_2(w)$, . . . or perhaps for values in a continuous range. To each value of q, say $q_n(w)$, there will correspond a characteristic function $r_n(x, w)$. The problem is thus reduced to a characteristic value problem of which only one solution will be physically significant; which solution this is will ordinarily be evident on consideration of the limiting case $w\to 1$. When the appropriate solutions $q(w)$ and $r(x, w)$ have been identified the mean contribution of each link to the extension of the chain may be computed in two ways:

$$\bar{x}(f) = d[\log q(e^f)]/df, \tag{6}$$

or

$$\bar{x}(f) = \int dx\{r(x, e^f)\}^2 x / \int dx\{r(x, e^f)\}^2. \tag{7}$$

For a chain with fixed valence angles and free rotation the integral equation becomes (with links of unit length)

$$q(w)r(x, w) = \int_{\mu x-(1-\mu^2)^{\frac{1}{2}}(1-x^2)^{\frac{1}{2}}}^{\mu x+(1-\mu^2)^{\frac{1}{2}}(1-x^2)^{\frac{1}{2}}} dy[1-x^2-y^2-\mu^2+2xy\mu]^{-\frac{1}{2}}e^{f(x+y)/2}r(y, w), \tag{8}$$

where $\mu = -\cos\psi$, ψ being the valence angle.

Solution of this integral equation with singular kernel presents serious difficulties. We have not yet succeeded in solving it in closed form, but have obtained a series solution which converges satisfactorily for extensions which are not extreme. Useful results can be obtained also by a process of successive approximations involving integrations of the form occurring in Eq. (8).

[1] H. M. James and E. Guth, J. Chem. Phys. 11, 455 (1943).

Application of Polya's Theorem to Optical, Geometrical, and Structural Isomerism

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September 17, 1943

IN a recent paper, T. L. Hill[1] has discussed the application of a theorem of G. Polya[2] to the calculation of the *total* number of isomers in compounds in which various substituents are attached to a rigid parent frame. For this purpose Hill considers only the group of rotational permutations of the points of the parent frame. Polya's theorem is more general than this, and may be used to enumerate separately the numbers of optical,[3] geometrical, and structural isomers in compounds of this type. The application to geometrical isomerism has not been stated explicitly by Polya.

Reference should be made to Hill's paper for definitions, and for the statement of Polya's theorem (Hill's Eq. (1)). One generalization is required: P may be *any* sub-group of order h, of the full group of $p!$ permutations on the p points, as in Polya's original proof.[2]

For a given type of substitution (k_1 substituents of a first kind, k_2 of a second kind, etc.), the non-equivalent configurations are those which are not superimposable by any permutation in P. Therefore, the number of non-equivalent configurations $A_{k_1k_2}\ldots$ is also the number of *isomers* of all types which are not superimposable by any of the covering operations represented by the particular sub-group P. The limiting cases[3] are illuminating; thus if P is the permutation which leaves each point unchanged, no two configurations may be superimposed, and each represents an isomer, while if P is the full group of $p!$ permutations, all the configurations may be superimposed and there is only one isomer for each type of substitution.

The calculation of the number of optical, geometrical, and structural isomers is effected by making the following choices of the sub-group P. It will be observed that the total number of isomers and the number of pairs of optical isomers depend only upon the symmetry of the parent frame, but that the division into geometrical and structural isomers depends also upon the particular molecule represented.

(i) If P is the sub-group of rotational permutations of the parent frame, $A_{k_1k_2}\ldots$ is the number of isomers which cannot be superimposed by rotation, that is, the total number of isomers.

(ii) If P includes, in addition to the rotational permutations of (i), the permutations corresponding to reflection of the parent frame in a plane, optical isomers become superimposable, and $A_{k_1k_2}\ldots$ is the number of structural and geometrical isomers.

(iii) For any given molecule, the set of p points may be partitioned into sub-sets, such that each sub-set is associated with (bonded to) a different atom in the parent frame. Let P be the product of the rotational and reflective sub-group of (ii) by the sub-group of permutations for which no points belonging in different sub-sets occur in the same cycle. Then the configurations representing geometrical isomers are superimposable, and $A_{k_1k_2}\ldots$ is the number of structural isomers.

As an illustration, consider cyclopropane, for which $p=6$, and there are 3 sub-sets of 2 points each. The symmetry formulas for the three cases are:

(i) $$\Sigma A_{k_1k_2}\ldots x_1^{k_1}x_2^{k_2}\cdots=(1/6)(f_1^6+3f_2^3+2f_3^2)$$

(ii) $$\Sigma A_{k_1k_2}\ldots x_1^{k_1}x_2^{k_2}\cdots=(1/12)(f_1^6+3f_1^2f_2^2+4f_2^3+2f_3^2+2f_6^1)$$

(iii) $$\Sigma A_{k_1k_2}\ldots x_1^{k_1}x_2^{k_2}\cdots=(1/48)(f_1^6+3f_1^4f_2^1+9f_1^2f_2^2+7f_2^3+8f_3^2+6f_1^2f_4^1+6f_2^1f_4^1+8f_6^1).$$

TABLE I. Number of isomers for substituted cyclopropanes.

Type of Isomer	Type of Substitution										
	1	x_1	x_1^2	x_1x_2	x_1^3	$x_1^2x_2$	$x_1x_2x_3$	$x_1^2x_2^2$	$x_1^2x_2x_3$	$x_1x_2x_3x_4$	$x_1x_2x_3x_4x_5$
(i)	1	1	4	5	4	10	20	18	30	60	120
(ii)	1	1	3	3	3	6	10	11	16	30	60
(iii)	1	1	2	2	2	3	4	5	6	9	15

On making the substitutions $f_1=(1+x_1+x_2+x_3+x_4+x_5)$, $f_2=(1+x_1^2+x_2^2+\cdots)$, $f_3=(1+x_1^3+\cdots)$, $f_4=(1+\cdots)$, and $f_6=(1+\cdots)$, and collecting like powers of x_1, x_2, $\cdots$, the coefficients shown in Table I (numbers of isomers) are obtained for the terms shown (representing all the possible types of substitution).

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[1] T. L. Hill, J. Chem. Phys. **11**, 294 (1943).
[2] G. Polya, Comptes rendus **201**, 1167 (1935).
[3] G. Polya, Zeits. f. Krist. **93**, 415 (1936).

Potential Barriers in Ethyl Alcohol and the Equilibrium in the Reaction $C_2H_4+H_2O\rightleftarrows C_2H_5OH$

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October 15, 1943

RECENT work on a general, empirical method to calculate potential barriers hindering internal rotation[1] enables us to estimate the barriers in ethyl alcohol. Figure 1 is a graph of the potential energy of the hydroxyl group as it rotates in ethyl alcohol.

No accurate treatment of the energies of such a system has been worked out but physical intuition leads one to a treatment analogous to that used for *n*-butane.[2] * This treatment leads to a "separation" of the molecule into two forms, "straight" ($\theta=0$ in Fig. 1) and "bent" ($\theta=104°$, 256° in Fig. 1). The "bent" form can, of course, exist in two optical isomers.

We do not wish to imply that ethyl alcohol actually exists in two distinct molecular forms. The procedure is simply a device for obtaining an approximate partition function corresponding to Fig. 1.

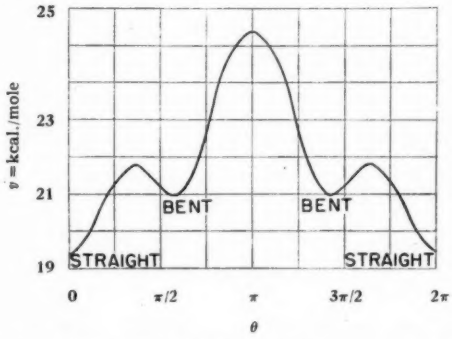

FIG. 1. The potential energy of the hydroxyl group in ethyl alcohol.

The difference in $E_0°$ (heat of formation at the absolute zero) is calculated to be 1560 cal./mole, the "bent" form having the higher energy, as is illustrated in Fig. 1. The "composition" has to be estimated at each temperature from

$$\Delta F° = +\Delta E_0° + \Delta(F° - E_0°).\dagger$$

The calculations were based on those of Schumann and Aston.[3, 4] The same "average" moment was used for both forms together with the previous vibrational assignment; the only change made in the frequency assignment was the use of 985 cm^{-1} [5] for the average of the six δ frequencies, instead of 905 cm^{-1}.

The following values have been used in the calculations for restricted rotation [1]

"Straight" form: CH_3 $V = 1800$ cal.
OH $V = 2375$ cal.
"Bent" form CH_3 $V = 3000$ cal.
OH $V = 4410$ cal.
I_{red} $CH_3 = 4.83 \times 10^{-40}$ g cm^2
OH $= 1.40 \times 10^{-40}$ g cm^2.

The barriers for the methyl group were estimated by the empirical treatment. The calculation and comparison of the entropies are summarized in Table I.

The equilibrium in the reaction

$$C_2H_4\,(g) + H_2O\,(g) \rightleftharpoons C_2H_5OH\,(g)$$

has been discussed previously.[3, 4]

The new value used for $\Delta E_0°$ is $-52{,}090$ cal./mole. Using this value in conjunction with the data for ethylene and water, the free energy changes recalculated at several temperatures are summarized in Table II. The agreement between the experimental and calculated values is excellent. Although the previous agreement[3] confirmed the presence of hindering potentials, the curves for experimental and calculated log K crossed. The new values show no such trend.

It is probably significant that the removal of the necessity for ridiculously high barriers for the hydroxyl group has resulted in a better agreement with experiment. Obviously every case with an unsymmetrical barrier should at least be treated in this approximate fashion, e.g., acetic acid, compounds with one unsymmetrical rotating group substituted in ethane, etc.

TABLE I. The entropy of ethyl alcohol from molecular data.

	351.5°K		403.2°K	
	Straight	Bent	Straight	Bent
S_{T+R}	61.03	62.41*	62.20	63.58*
S_{vib}	2.77		3.85	
$S_{f(CH_3)}$	3.67		3.80	
$S_{f(OH)}$	2.44		2.58	
$(S-S_f)_{CH_3}$	−0.58	−1.15	−0.48	−0.96
$(S-S_f)_{OH}$**	−0.71	−1.37	−0.59	−1.24
S	68.62	68.77	71.36	71.61
% present	88	12	84	16
Mixing	0.73		0.87	
$S°_T$	69.4		72.3	
3rd law entropy	69.8		72.1	

* S_{T+R} includes the entropy of mixing for the optical isomers but does not include the rotational entropy of the methyl or hydroxl groups.

** $S_f = R(-0.775 + \frac{1}{2}\ln T + \frac{1}{2}\ln I_{red} \times 10^{40} - \ln n)$. Placing $n = 3$ limits the rotation to one-third of a revolution.

TABLE II. The free energy change and the equilibrium constant in the reaction $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$.

	Experimental		Calc.(Previous†)		Calc.(This Research)	
T°K	$\Delta F°$	$\text{Log}_{10}K$	$\Delta F°$	$\text{Log}_{10}K$	$\Delta F°$	$\text{Log}_{10}K$
298.2	−1200	+0.88	−1630	+1.20	−1565	+1.17
351	+ 315	−0.20	− 350	+0.22	+ 15	−0.01*
403	+1800	−0.98	+1570	−0.85	+1570	−0.85*
600	+7480	−2.72	+7700	−2.80	+7488	−2.72

* Obtained by interpolation.
† See reference 4.

A similar treatment of the *n*-hydrocarbons leads to the conclusion that the amount of "bent" form in the gas phase is negligible[6] in agreement with the infra-red data.[7]

Such a result is not in conflict with the thermodynamic data which can be made to agree on this basis as well as that of Pitzer.[2]

[1] Aston, Isserow, and Kennedy, to be published shortly. This method predicts all the known barriers for the methyl groups within experimental error for simple molecules including tetramethylmethane and silicontetramethyl.
[2] Pitzer, J. Chem. Phys. **8**, 711, (1940).
* All unsymmetrical barriers should be treated by essentially this method.
[3] Schumann and Aston, J. Chem. Phys. **6**, 480 (1938).
[4] Aston, Ind. Eng. Chem. **34**, 514 (1942).
[5] Dailey and Felsing, J. Am. Chem. Soc. **65**, 44 (1943).
† Pitzer takes $\Delta F° = \Delta E_0°$ for *n*-butane, reference 2.
[6] A communication on this subject will appear shortly.
[7] Whitcomb, Nielsen, and Thomas, J. Chem. Phys. **8**, 143 (1940).

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CONTENTS

THE JOURNAL OF CHEMICAL PHYSICS VOL. 11, NO. 11 NOVEMBER, 1943

Crystal Structure of Silver Oxalate . . . . . S. C. Gurney 499

Kinetics of the Oxidation of Isopropyl Alcohol by Chromic Acid . . . . . F. H. Westheimer and Alfred Novick 506

Statistical Mechanics of Cross-Linked Polymer Networks. I. Rubberlike Elasticity . . . . . Paul J. Flory and John Rehner, Jr. 512

Statistical Mechanics of Cross-Linked Polymer Networks. II. Swelling . . . . . Paul J. Flory and John Rehner, Jr. 521

Statistical Thermodynamics of Rubber. III . . . . . Frederick T. Wall 527

Letters to the Editor:

Infrared Transitions of Symmetrically Diatomic Crystals . . . Hubert M. James and Bernard Kohn 536

Application of Polaron Theorem to Optical, Paramagnetic, and Structural Interactions . . . . . William J. Carter 538

Potential Barriers in Space Among Isomeric Substituents in the Reaction $C_2H_5 + H_2O_2 \rightarrow C_2H_5OH$ . . . . . John G. Aston, Gilbert J. Szasz, and Sam Isserow 539

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